Kinetic-free selectivity control of chemical reactions leading to nonvolatile products

Francesco Maestri, Renato Rota *

Politecnico di Milano, Dip. di Chimica, Materiali e Ingegneria Chimica "G. Natta", via Mancinelli 7, 20131 Milano, Italy

HIGHLIGHTS

- A number of reaction processes undergo selectivity losses due to by-products formation.
- Using a semibatch recycle reactor (SBRR) allows achieving both high selectivity and productivity.
- For fine chemical and pharma processes the kinetic parameters are often unknown.
- A criterion is proposed to identify optimal SBRR conditions without knowing any kinetic parameters.

ARTICLE INFO

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 nonselective 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 noncontinuous 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.

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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 nonselective 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 nonselective reactant, A:

$$A + B \overset{k_1}{\Longrightarrow} C$$

$$A + C \overset{k_2}{\Longrightarrow} D \qquad (1)$$
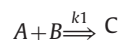
The undesired consecutive reaction is typically of the same class as the main one: therefore, the enthalpies of the two reactions are normally close to each other.

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 olygo-meric species; moreover, dealing with electrophylic substitution

* Corresponding author. Fax: +39 0223993180.
E-mail address: renato.rota@polimi.it (R. Rota).

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, $m^3/(kmol\ s)$
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
$\tilde{Q}$	$\dot{Q}/(UA)_{0,t}T_R$, dimensionless heat duty, –
r	reaction rate, $kmol/(m^3\ s)$
R	gas constant $= 8.314$, $kJ/(kmol\ K)$
R_H	heat capacity ratio, –
R_x	t_{dos}/τ, recycle number, –
S	normalized sensitivity parametric coefficient, –
S_y	$(Da \cdot \kappa)_1/(Da \cdot \kappa)_2$, selectivity number, –
St_t	$(UA)_{0,t}t_{dos}/(\tilde{\rho}\tilde{C}_P)_r V_r$, modified Stanton number, –
t	time, s
T	temperature, K
$\tilde{T}$	T/T_R, dimensionless temperature, –
U	overall heat transfer coefficient, $kW/(m^2\ K)$

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
$\Delta\tilde{T}_{ad}$	$C_{B0,r}(-\Delta\tilde{H})/(\tilde{\rho}\tilde{C}_P)_r T_R$, 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, –

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 nonselective) 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.

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 Fig. 1 (Maestri and Rota, 2013), both a satisfactory process

selectivity and productivity can be achieved, even in a noncontinuous plant.

The SBRR process configuration consists of a top stirred tank reactor, to which the nonselective 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, 1990) and adopting a sufficiently high recycle rate of the reactant B through the system, the nonselective 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 nonselective reactant dosing time as well as much higher than the average residence time in the reactor.

However, the application of the criterion presented in Maestri and Rota (2013) requires the knowledge of the kinetic parameters