Development and validation of a simple and cost effective procedure for scaling-up hazardous chemical processes

Copelli S., Maestri F., Rota R.
Politecnico di Milano - Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta",
Via Mancinelli 7, 20131 Milano, Italy
fax: +39 0223993180; e-mail: renato.rota@polimi.it

Lunghi A., Gigante L., Pasturenzi C., Dellavedova M., Cardillo P.
Stazione Sperimentale per i Combustibili
V.le A. De Gasperi 3, 20097 S. Donato Milanese (MI), Italy

In this work scale-up of hazardous chemical processes, carried out in indirectly cooled semibatch reactors (SBRs), is approached using a simple and general criterion arising from a generalized form of boundary and temperature diagrams, already presented in the literature. In order to scale-up a reaction process, the first type of diagrams is used to minimize dosed reactant (coreactant) accumulation in the system (by verifying that, under the selected operating conditions, system's reactivity, R_y, is above an inherently safe threshold value, $R_{y,QFS}$); the second one, instead, allows to optimise process parameters, identifying optimum operating conditions, for what concerns both reactor's safety and productivity.
In order to validate the aforementioned safety and scale-up criterion, the nitration of 4-chloro benzotrifluoride (4-Cl BTF) has been analyzed.

1. Introduction

In the fine chemical and pharma industry, semibatch reactors (SBRs) are normally employed to perform relatively fast and exothermic reactions.
Such reactors have frequently been involved in industrial accidents with disastrous consequences (e.g. Seveso, 1976 and Bhopal, 1984) (Cardillo, 1998).
The main cause of these events is the loss of control of reactor's temperature with further triggering of either unwanted side reactions or decompositions of the reacting mixture, that can lead to further increases of reactor temperature. This phenomenon, known as "thermal runaway", represents one of the most important problems when scaling-up a process. In fact, because of the increase of reactor's volume when moving from laboratory to industrial scale, the ratio between heat removed by the cooling system (proportional to the square of the equipment characteristic dimension) and heat evolved by the reaction (proportional to the cube) decreases.
In this work the 4-Cl-3-nitro BTF synthesis (carried out in liquid-liquid SBRs) has been studied in order to validate a productive and cost effective safe scale-up procedure which, through the use of two different typologies of generalized diagrams (Maestri and Rota, 2005 - 2006), optimises the most important operating parameters for a semibatch reactor: namely, the dosing time.

2. Performed experiments

The synthesis of 4-Cl-3-nitro BTF is industrially performed in liquid-liquid SBRs, according to the following reaction:

$$ClC_6H_4CF_3 + HNO_3 \rightarrow ClC_6H_3(NO_2)CF_3 + H_2O \quad (1)$$

The reaction takes place in the acid phase through a nitronium ion (NO_2^+) mechanism, at sulphuric acid concentrations above 90% (to which an NO_2^+/HNO_3 concentration ratio close to one corresponds).
A number of experiments have been carried out in order to validate the use of the criterion in question.

In particular three different typologies of tests have been performed:

1) a thermal stability test, performed through an Accelerated Rate Calorimeter (ARC) equipment, in order to determine a temperature threshold value, successively called MAT (Maximum Allowable Temperature) beyond which a strongly exothermic and gas producing decomposition of the reaction mass or unwanted side reactions may occur;
2) an adiabatic test, performed through an RC1 calorimeter, aimed to determine the microkinetic rate of reaction expression;
3) two isoperibolic tests, performed in an RC1 equipment, through which the safety and scale-up criterion has been validated.

Accelerating Rate Calorimeter (ARC) test
The ARC equipment is an adiabatic calorimeter controlled by a microprocessor and a data system of analysis. Such a calorimeter is typically used to analyze reacting systems that can undergo decomposition events.
After the 4-Cl-3-nitro BTF synthesis has been performed in a stirred glass flask, a sample of the final reaction mass has been loaded into the ARC sample holder. Then a standard Heat – Wait – Search cycle has been started.
Table 1 summarizes the results obtained.

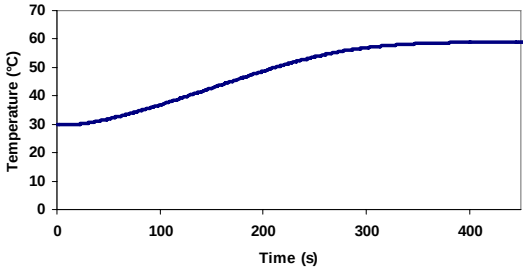
Table 1 Summary of the results obtained by ARC test runs on final reactive mixture.

Decomposition effect of the reactive mixture
Initial effect temperature, T_0 (°C) = 141
Final instrumental temperature, T_{fin} (°C) = 255.45
Instrumental adiabatic temperature rise (°C) = 114.1
Instrumental inertia factor, **Φ**= 2.846
Correct adiabatic temperature rise (°C) = 324.8
Correct final temperature (°C) = 465.8

Reaction calorimeter (RC1) tests

In order to determine the microkinetic rate of reaction expression, an adiabatic RC1 test has been carried out, in which 4-Cl-BTF has been instantaneously added to the mixed acids at 500rpm stirring speed and employing a diluted recipe: namely, using an excess of sulphuric acid in the mixed acids mixture. This variation with respect to the industrial process does not imply any approximation on the real microkinetics, but it is necessary to avoid decomposition phenomena of the reacting mixture and to obtain the desired slow operating reaction regime. Figure 1 shows the adiabatic temperature – time profile obtained.

Figure 1 RC1 Adiabatic temperature profile for the synthesis of 4-Cl-3-nitro-BTF.



The microkinetic rate of reaction expression has been obtained introducing temperature vs. time data into a suitable fitting software:

$$r = 3.228e+12 \cdot e^{\left(-\frac{87260}{8.314T}\right)} C_{BTF} C_{HNO_3} \qquad (2)$$

with: $A = 3.228e+12$ [m^3/(kmol s)], $E_{att} = 87260$ [J/mol] and C_{BTF/HNO_3} [kmol/m^3].

Isoperibolic tests

In order to verify the applicability of boundary and temperature diagrams two isoperibolic tests have been performed.

The operating conditions have been chosen through temperature and boundary diagrams. The two following sets of process parameters have been analyzed:

- isoperibolic test at a coolant temperature equal to 308 K (to which a sufficiently low coreactant accumulation corresponds);
- isoperibolic test at a coolant temperature equal to 305 K (to which an excessive coreactant accumulation corresponds).

In both cases maximum reactor temperature has been estimated through temperature diagrams to be far from the MAT value.

In order to verify the conclusions drawn through the usage of boundary and temperature diagrams, a check has been performed on:

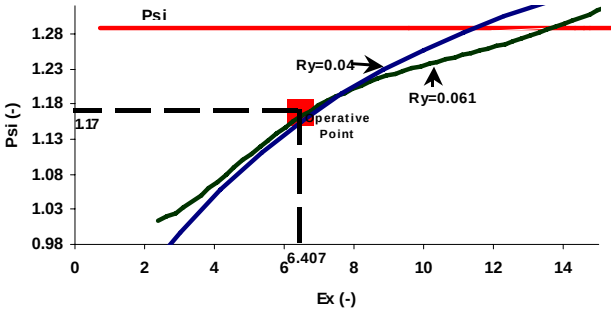
- maximum temperature reached by the system under isoperibolic conditions;
- coreactant accumulation at the end of dosing time.

From the corresponding temperature rise curves and at the current exothermicity numbers, $E_{x,308}$ and $E_{x,305}$, reporting the (T_{max}/T_0) values determined in the isoperibolic tests (see Figure 2), it can be verified that:

$$\Psi < (\frac{MAT}{T_0} = \Psi_{MAT}) \tag{3}$$

Therefore, in both the analyzed sets of operating conditions, the system does not undergo decomposition phenomena because both the theoretical and experimental ψ values are lower than the correspondent ψ_{MAT} value. Moreover, the experimental ψ value is lower than the theoretical one, showing that the model leads to safe conclusions.

Figure 2 Temperature diagram for the 308 K case. Parametric curves ψ= ψ(E_x) has been calculated at R_y=0.0533 and $R_{y,QFS}$=0.063.



From the boundary diagram for the 308 K case and representing the operating point of the system (that is, calculating the $E_{x,308}$ and $R_{y,308}$ values), it has been found that the process would be carried out under safe conditions, since the operating point is outside the Excessive Accumulation Region (EAR).

Integrating the calorimetric conversion curve, calculated by the RC1 software, it has been determined that, at the end of the dosing period, 95% of 4-Cl-BTF has been consumed.

From the boundary diagram for 305 K case and representing the operating point of the system ($E_{x,305}$ and $R_{y,305}$), it has been found that it falls into the runaway region. A check on the accumulation of the coreactant into the system allows to verify that, at the end of the dosing time, the conversion is only 92%.

This means that operating into the runaway region implies a higher coreactant accumulation. This is in perfect agreement with what is stated by the developed mathematical model.

It is therefore possible to identify optimum laboratory operating conditions using two generalised form of boundary and temperature diagrams, namely:

- an Inherently Safe Conditions diagram (ISC), calculated for the appropriate typology of reaction (in this case: liquid-liquid slow reactions occurring in the continuous phase) to evaluate $R_{y,QFS}$ at the current Co value (see Figure 3);
- a generalized Temperature Rise Curve diagram (TRC) in order to evaluate the maximum temperature increase with respect to the initial reactor temperature at the current exothermicity value and for all the possible Co, R_H, n and m values (see Figure 4).

An isoperibolic RC1 test has been finally performed in order to verify the identified optimum laboratory operating conditions. From Figures 3 and 4 it is possible to observe that safe and productive operating conditions have been achieved. A further check is the calculation of calorimetric conversion at the end of the dosing period which resulted to be 98%.

Figure 3 ISC diagram and optimum operating point as individuated from isoperibolic RC1 test.

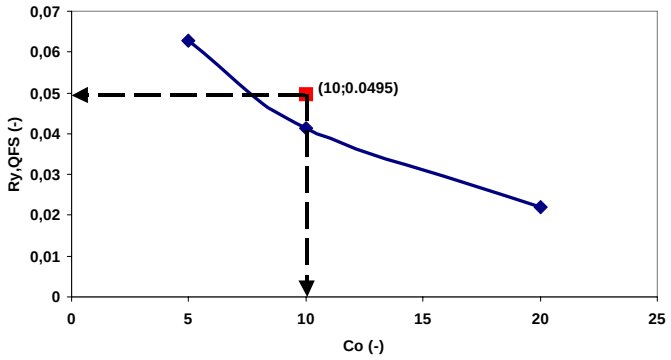
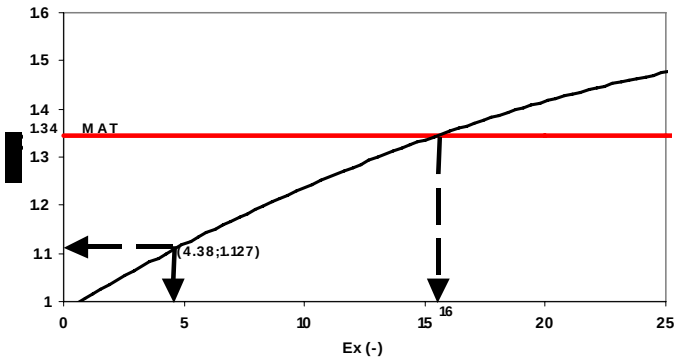


Figure 4 TRC diagram and actual temperature increase with respet to the initial RC1 temperature for the isoperibolic test performed. It is also indicated the maximum exothermicity number acceptable at the industrial scale (in this case: 16).



In Table 2 the identified optimum conditions at the laboratory scale are summarized.

Table 2 Optimum laboratory operating conditions individuated using ISC and TRC diagrams.

Initial temperature, T_0	308 K	Co	10	$\nu_A DaRE$	0.0580349
Coolant temperature, T_{cool}	308 K	R_H	0.445	ε	0.333297
Dosing time, t_D	1066 s	n	1	γ	34.98837303
Tmax	400 K	m	1	$\Delta\tau_{ad,0}$	0.4147695

3. Scale-up procedure

Generalized Temperature Rise Curve and Inherently Safe Conditions diagrams may be employed to scale-up, from the laboratory to the industrial scale, a generic exothermic semibatch process: in particular an heterogeneous one with reaction occurring in the continuous phase. The scale-up strategy consists in the following steps:

a) calorimetric screening tests, that is:

- DSC tests on reactants and products in order to characterize their thermal behaviour into a suitable temperature range;
- thermal stability tests on the reacting mixture using the ARC adiabatic calorimeter, in order to identify the MAT parameter for the analysed system;
- adiabatic tests at different stirring speeds using ARC, PHI-TEC II or RC1 equipments, in order to determine the microkinetic rate expression (even for homogeneous systems).

b) fitting of the experimental data obtained from adiabatic tests and estimation of the reaction microkinetic parameters;

c) use of ISC and TRC diagrams to identify optimal laboratory (that is, at the RC1 scale) operating conditions. In particular the following constraints must be fulfilled:

$$\Psi_{max} T_0 < MAT \tag{4}$$

$$R_y \geq R_{y,QFS} \tag{5}$$

d) use of ISC and TRC diagrams to scale-up process operating conditions. This scale-up strategy is based on dimensional parameters characterizing the process and, in particular, on the main process variables subjected to change during the scale-up process: namely, initial reaction temperature, T_0, and dosing time, t_D.

Since the initial reaction temperature arises mainly from the chemical recipe than with respect to safety and product quality constraints, the scale-up procedure in question is based on dosing time, t_D, as the only process parameter at plant operator's disposal.
In the scale-up process it is crucial that every variation of process variables is inherently safe. When moving from laboratory to full plant scale, it is evident that dosing time increases. However, in order to maximize the reactor productivity, we are interested in limiting as much as possible the dosing time increase, under safe conditions. Such a problem can be easily solved through the general temperature rise curve of Figure 4: from the ψ value corresponding to the MAT for the process in question, ψ_{MAT}, and taking into account that ψ is an increasing function of E_x, it is possible to read off the corresponding $E_{x,MAX}$ value, which is the maximum value of exothermicity number that, at the industrial scale, can be accepted, according to the MAT constraint. Since all the other dimensionless parameters appearing in E_x, but Co, are not subjected to any variation during the scale-up process, to the aforementioned $E_{x,MAX}$ value a minimum value of the cooling number and finally (being physical and heat transfer characteristics of the reactor known) a minimum dosing time at the full plant scale corresponds. As a difference with respect to a dimensionless scale-up procedure, which keeps Co constant moving from laboratory to industrial scale, in this case a cooling number decrease is not only accepted but also maximized, in order to minimize the dosing time on industrial reactor and hence to maximize its productivity.
So from $E_{x.MAX}$ determined it has been calculated maximum cooling number for industrial 4-Cl-BTF nitration reactor and hence, knowing heat transfer properties of the system (namely, UA_0), determine minimum industrial dosing time.

$$E_{x,MAX} = \frac{\gamma}{\tau_{cool}^2} \frac{\Delta\tau_{ad,0}}{\varepsilon\left(Co_{MIN} + R_H\right)} \Rightarrow Co_{MIN} \qquad (6)$$

$$Co_{MIN} = \frac{1}{\tilde{\rho}_c \tilde{C}_{p,c}} \cdot \frac{(UA)_0}{V_{dosato}} \cdot t_{D,MIN} \Rightarrow t_{D,MIN} \qquad (7)$$

By optimising $t_{D,MIN}$, even considering other constraints, as pumping power, optimum industrial dosing time is calculated.

$$t_{D,MIN} \Rightarrow t_{D,opt} \qquad (8)$$

Table 3 summarised the results obtained for the case analysed.

Table 3 Result obtained for 4-Cl-3-nitro BTF synthesis scale-up.

$E_{x,MAX}$	16
Co_{MIN}	2.14
$t_{D,MIN}$ (s)	2146
$t_{D,opt}$ (s)	3863

7. Conclusions

In this work the scale-up problem of processes carried out in semibatch reactor (operating in isoperibolic conditions and involving heterogeneous liquid – liquid reactions) has been faced, through the use of two different typologies of diagram: temperature rise curve and inherently safe conditions diagrams.
In order to validate the scale-up procedure, a number of experimental tests, relative to 4-Cl-3-nitro BTF synthesis, have been performed.
The obtained results have shown that the temperature rise curve and the inherently safe conditions diagrams are suitable tools to characterize the thermal behaviour of an heterogeneous SBR, allowing for the optimisation of the main operating parameters of a SB process: namely, the dosing time, t_D .

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