



Safe and Selective Operation of Fine Chemical Reactions through the Semi Batch Recycle Reactor (SBRR)

Francesco Maestri^{*a}, Carlo Pirola^b, Renato Rota^a

^aPolitecnico di Milano - Dip. di Chimica Materiali e Ingegneria Chimica, Piazza Leonardo da Vinci 32 - 20133 Milano, Italy

^bUniversità degli Studi di Milano - Dipartimento di Chimica, Via Golgi 19 - 20133 Milano, Italy

francesco.maestri@polimi.it

In the fine chemical industry, a number of exothermic reaction processes are better performed under reflux conditions. Such an operating regime of the reactor allows for removing the reaction heat at a self-controlling temperature, hence preventing peaks of the conversion rate with their related thermal effects. Moreover, when the desired reaction generates a low volatility product, which can further react with a non-selective reactant, dosing such a reactant under reflux conditions potentially allows for removing the target species from the reactor, hence subtracting it from its further degradation.

However, there exist also a number of processes that must be operated at temperature values lower than the normal boiling point of the low volatility product and for which vacuum conditions cannot be adopted, because of a number of process constraints. This prevents the possibility of taking advantage, from a safety point of view, of the aforementioned self-controlling feature of the processes operated under reflux conditions.

The semibatch recycle reactor allows for achieving both a satisfactory process selectivity and productivity (strictly connected with the operating temperature range defined by the recipe) as well as the safer process conditions related to the reflux conditions thanks to its intrinsic possibility of operating even at atmospheric pressure the reaction vessel and the boiler at different temperature values.

1. Introduction

In the fine chemical industry a number of fast and exothermic reaction processes can be encountered, for which a gradual conversion of the reactants into the products is recommended (Steensma and Westerterp, 1988, 1990; Steinbach, 1999; Copelli et al. 2010): this because an uncontrolled temperature rise could cause a thermal runaway with serious injuries to the plant and to the people working on it. The same occurs when dealing with reaction processes generating corrosive gases (such as hydrogen chloride), which evolution must be spread over a suitable time period, in order to limit the load to the subsequent absorption units.

Among this broad class of hazardous processes there are some chemical processes undergoing selectivity problems since an intermediate target species can unselectively react with one of the reactants to yield heavier by-products (Garner and Nunes, 1973; Arpe, 2010).

In these cases, performing the reaction process under reflux conditions can be a winning solution for both safety (since the potentially dangerous self-accelerating behaviour of temperature is better controlled by the latent heat of evaporation) and selectivity (thanks to the continuous separation of a target product from the reaction mixture that effectively prevents its further degradation: the reflux conditions allow a continuous removal of the low volatility target species from the reaction mixture as bottom product).

However, if the reaction temperature given by a specific process recipe is lower than the attainable reflux temperature of the system at atmospheric pressure, the system should be operated under vacuum, leading to other problems related to both an increase of the cost as well as to possible vacuum leakages creating further safety problems (for instance, those related to a catalyst deactivation due to oxygen in air with the following coreactant accumulation in the system). In other words, this prevents the possibility of taking advantage, from a safety point of view, of the self-controlling feature of the processes operated under reflux conditions.

In these cases, the semibatch recycle reactor (SBRR) process configuration could be an interesting alternative since it allows for operating the reaction vessel and the boiler at different temperature values. Therefore, this intrinsic characteristic of the SBRR allows for achieving both a satisfactory process selectivity and productivity (strictly connected with the operating temperature window defined by the recipe) as well as the safer process conditions related to the reflux conditions.

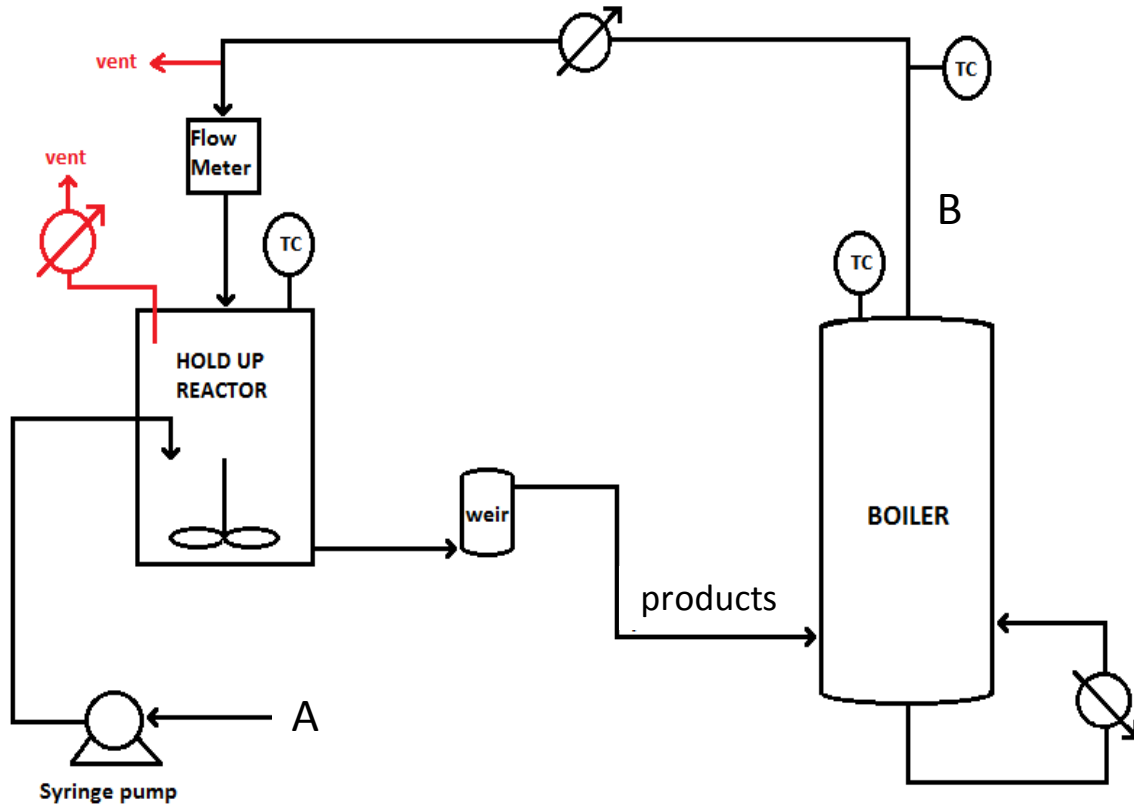


Figure 1: SBRR process configuration

In this work the main advantages and limitations related to the use of a SBRR with respect to a standard SBR are discussed using an industrial relevant industrial process recently investigated experimentally (Rota and Maestri, 2018) as a case-study.

2. Results and discussion

Assume that a low volatility target product C can unselectively react with a dosed reactant A from which it has been previously generated through reaction with a species B, according to the scheme:



In these cases the semibatch recycle reactor sketched in Figure 1 can be used to achieve both a high process selectivity and productivity as discussed elsewhere (Maestri and Rota 2013 and 2015). According to such a plant configuration the selective reactant B is refluxed at a given rate between a top reaction vessel and a bottom reboiler, where the separation between target product C and unreacted B occurs.

The coreactant A is dosed in the top reactor at a relatively low rate, hence minimizing the accumulation of C in the reactor and subtracting it from its further reaction with A, even at a relatively low initial excess of the selective reactant B.

The mathematical model describing this plant configuration consists of a set of three Ordinary Differential Equations (ODEs) describing the time evolution of the B reactant conversion:

$$\chi = \frac{n_{B0} - n_B}{n_{A1}} \quad (2)$$

of the B reactant selectivity to product C:

$$\sigma = \frac{n_C}{n_{B0} - n_B} \quad (3)$$

and of the dimensionless concentration of product C in the top reactor, $\gamma_{C,r}$:

$$\gamma_{C,r} = \frac{C_{C,r}}{C_{B0,r}} \quad (4)$$

The dimensionless ODEs are the following (see for the detailed derivation of the mathematical model Maestri and Rota, 2013 and the related Supporting Information section):

$$\frac{d\chi}{d\vartheta} = Da_1 \frac{1}{Ex^{n-1}} [\vartheta - \chi(2 - \sigma_C)]^n \left(1 - \frac{\chi}{Ex}\right)^m \kappa_1 \quad (5)$$

$$\begin{aligned} \frac{d\sigma_C}{d\vartheta} = & Da_1 \frac{1}{Ex^{n-1}} \frac{1}{\chi} [\vartheta - \chi(2 - \sigma_C)]^n \left(1 - \frac{\chi}{Ex}\right)^m \kappa_1 + \\ & - Da_2 \frac{1}{Ex^{p-1}} \frac{1}{\chi} [\vartheta - \chi(2 - \sigma_C)]^p \gamma_{C,r}^q \kappa_2 - \frac{\sigma_C}{\chi} \frac{d\chi}{d\vartheta} \end{aligned} \quad (6)$$

$$\frac{d\gamma_{C,r}}{d\vartheta} = Da_1 \frac{1}{Ex^n} [\vartheta - \chi(2 - \sigma_C)]^n \left(1 - \frac{\chi}{Ex}\right)^m \kappa_1 - Da_2 \frac{1}{Ex^p} [\vartheta - \chi(2 - \sigma_C)]^p \gamma_{C,r}^q \kappa_2 - R_x \gamma_{C,r} \quad (7)$$

with initial conditions at $\vartheta=0$: $\chi=0$, $\sigma_C=1$ and $\gamma_{C,r}=0$.

In these equations, $Da_1 = k_{1,R} t_{dos} C_{B0,r}^{n+m-1}$ and $Da_2 = k_{2,R} t_{dos} C_{B0,r}^{p+q-1}$ are the Damköhler numbers for the main and the side reaction, that is the ratio of the dosing time to the characteristic time of each reaction; $\kappa_1 = \exp[\gamma_1(1 - T_R/T_r)]$ and $\kappa_2 = \exp[\gamma_2(1 - T_R/T_r)]$ are the dimensionless reaction rate constants; $R_x = t_{dos}/\tau$ is the recycle number, that is the ratio of the dosing time to the average residence time in the top reactor; Ex is the effective excess number, that is, the ratio of the initial hold-up of B in the reactor to the overall amount of A to be dosed (for a 1:1 stoichiometry). After the supply period (that is, at $\vartheta > 1$), the ϑ terms in the right hand sides of Equations (5) to (7) must be replaced by one.

The energy balance of the system has not been reported here, since the reaction occurs under isothermal conditions in the top vessel: the energy balance can therefore be separately solved in order to calculate the net heat removal rate from the system, as difference between the heat removal rate at the top condenser and the heat supply rate at the bottom reboiler (see Maestri and Rota, 2015).

Solving equations (5) to (7), the general behaviour of a SBRR with respect to a standard SBR in terms of process selectivity can be easily illustrated. For the sake of example, in Figure 2 the asymptotic selectivity to C vs. the adopted dosing time of A is plotted at a negligible and finite reflux rate of B, the former corresponding to the limiting case of a SBR system.

As can be noticed, operating the system under recycle conditions of B (that is, performing the reaction in a SBRR), acts to remove the product C from the reactor with a consequent recovery of selectivity. In fact, if the target product C is generated at a higher time scale than its average residence time in the reactor, the undesired reaction between the fed reactant A and the target species C is at the limit suppressed.

In fact, increasing the coreactant dosing time in a standard SBR system the accumulation in the reactor occurs within a mixture of B and C, and the fed coreactant A can therefore unselectively react with both. For this reason, the final selectivity to C quickly drops to an asymptotic lower limit. Instead, increasing the coreactant dosing time in a SBRR system operated at a given reflux rate of B leads to a more effective segregation between A and C and therefore to a selectivity recovery.

The SBRR process configuration allows therefore for operating the reactor continuously even within a non-continuous system and with the possibility of setting the residence time in a much more flexible way.

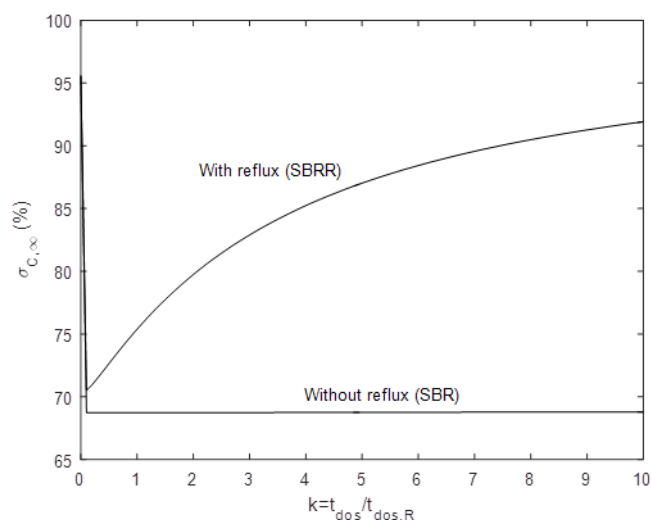
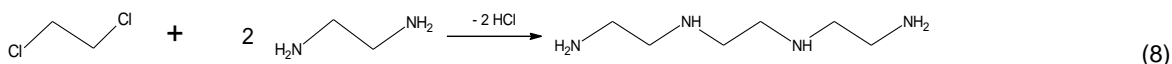


Figure 2: SBRR selectivity behavior without and with internal reflux.

$Ex=1.5$; $\gamma_1=\gamma_2=30$; $n=m=p=q=1$; $T/T_R=1.1$; $Da_1=Da_2=1$ at $t_{dos}=t_{dos, R}$.

Moreover, as previously mentioned, the SBRR plant configuration allows for setting the temperature of the main reactor vessel and of the boiler at different values. In particular, while the boiler operates at the mixture boiling point (since the species B must be separated from the mixture through a distillation process), the reactor temperature can be set at a different temperature value.

The superior performances of the SBRR plant configuration with respect to the SBR ones has been recently demonstrated experimentally (Maestri et al., 2018) for a non-continuous non-selective synthesis of valuable product through a reaction between a reactant with a non-selective dosed co-reactant, that is the synthesis of triethylenetetramine (TETA) through reaction of ethylenediamine (EDA) with 1,2-dichloroethane (DCE):



In this case EDA is refluxed through the system and DCE is dosed in a suitable time. Performing the reaction in question under reflux conditions in a SBR at atmospheric pressure is not possible since the EDA normal boiling point (116°C) is higher than the temperature at which the reaction must be performed (around 50-75°C). Moreover, operating the system under a controlled vacuum in order to match the reaction temperature with the reflux temperature could lead to an unexpected hydrogen chloride evolution, if it is not effectively neutralized by the EDA excess.

The SBRR process configuration is indeed able to provide a process configuration operating at atmospheric conditions through a split between boiler and reactor temperatures (through the condensate subcooling) and to remove the reaction heat at a self-controlling temperature under atmospheric conditions.

Moreover, the DCE/EDA alkylation system undergoes selectivity decays since DCE can further alkylate the target polyamine to generate heavier derivatives (Maestri et al., 2018). For these reasons the GC assay of TETA in the market is limited to 60%, the main impurities being reported in the technical data sheets of the leading producers (Huntsman, 2008). Therefore, the SBRR process configuration can achieve a higher process selectivity through an effective segregation of TETA from the further attack of EDA, as shown in Figure 3 where the results reported in Maestri et al. (2018) are recast in term of process selectivity versus DCE doing time for both the standard SBR and the SBRR plant configurations. We can see that the final process selectivity increases from about 50% the SBR experiments up to about 60% for the SBRR ones, that is 10% higher.

Therefore, the SBRR plant configuration can deal quite effectively with selectivity and productivity problems related to the standard SBR, as well as some safety problems related to vacuum conditions (such as the previously mentioned evolution of hydrochloric acid).

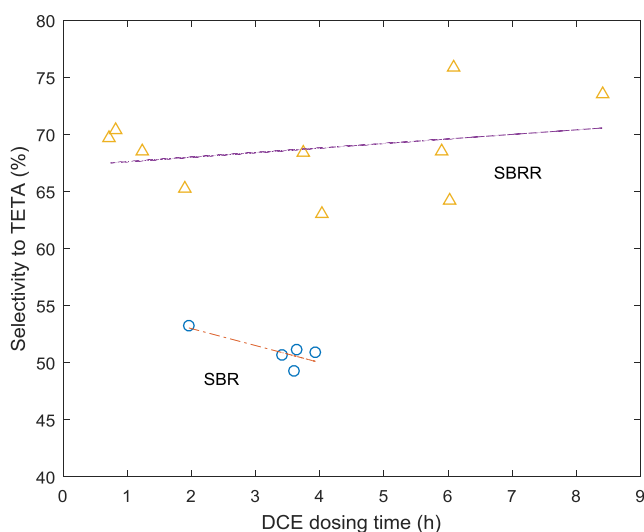


Figure 4: Process selectivity for SBR and SBRR experiments (data from Maestri et al., 2018)

However, there are several other advantages related to the SBRR plant configuration with respect to the standard SBR one. They are mainly related to the possibility of separating the reactor temperature value from that of the boiler, where the reactant B is continuously evaporated and, after condensation, continuously recycled to the reactor.

In particular, while in the SBR operating under isoperibolic conditions the cooling capacity of the reactor is designed to cope with the reaction enthalpy in order to limit the maximum temperature increase, in the SBRR the cooling capacity must be designed to remove not only the reaction enthalpy, but also the condensation heat of the recycled species. Therefore, when an accidental scenario leads to an increase in the SBR heat release rate, the cooling system hardly can cope with it and a runaway reaction is like to occur.

However, when the same unwanted heat release rate happens in a SBRR the only consequence is to lower the heat duty to keep the internal reflux rate at the set point value. The installed cooling power at the top condenser can still undercool the reflux to be recycled to the reactor (which does not change its rate) up to the same set point temperature, therefore avoiding any runaway triggering in the reactor. As a side advantage of using a SBRR plant configuration, we can also mention that the heat transfer coefficients at the top condenser are not influenced by any fouling phenomenon due to the reaction mass, contrary to the jacket cooler of a standard SBR.

Thanks to all these features, the SBRR process configuration allows for getting the maximum advantage in terms of safety from the reaction mass reflux, hence lowering the safety characteristics of the performed process, according to Stoessel (1993).

Performing the alkylation of EDA through DCE in a standard SBR operated at the proper reaction temperature (that is, 50-75°C) and at atmospheric pressure, if at any time the thermal loss of control of the system occurs, the reaction temperature rises at least up to the reflux temperature of EDA (that is, 116°C), whereas the reaction must be performed at 50-75°C. Therefore, under such conditions the unexpected boiling of unreacted DCE would take place.

In a SBRR system, instead, an increasing exothermic contribution of the reaction could be promptly faced reducing the heat input to the bottom reboiler and bringing the system at the same internal reflux rate at the limit through chemical reaction only. Therefore, the safe reactor operation would be suddenly recovered.

The same holds true if additional exothermic contributions appear, because e.g. of a plant failure: as an example, the accidental leakage of alkaline water into the system could be mentioned; in this case, in fact, an exothermic sudden reaction with the hydrochlorides of the amines would take place, with the related exothermic effect.

3. Conclusions

Several fine chemical reactions performed in semibatch reactors should be better performed under reflux conditions in order to operate at a self-controlled temperature. However, the recommended reaction temperature is in general different from the reflux temperature under atmospheric conditions and operating the

system under vacuum is not always possible because of a number of plant and process constraints. In this case the SBRR allows for performing the reaction under atmospheric reflux conditions at an independent reaction temperature.

Moreover, if at any time an unexpected exothermic contribution takes place in the system, through the SBRR configuration the process safety can be promptly recovered reducing the heat input to the bottom reboiler and hence sustaining the internal reflux at the limit through the exothermic contribution of the chemical reaction only.

The same process configuration is in particular useful when dealing with reaction processes for which a low volatility target species can unselectively react with the dosed reactant and must therefore be segregated from it. In this case, a significant recovery of process selectivity and productivity can be achieved.

References

- Arpe, H.J., 2010. *Industrial Organic Chemistry*, fifth ed. Wiley-VCH, Weinheim.
- Copelli, S., Derudi, M., Maestri, F., Rota, R., 2010, Safe Operating Conditions for Semibatch Processes Involving Consecutive Reactions with Autocatalytic Behaviour. *Chem. Eng. Sci.* 65, 5464-5470.
- Garner, P.J., Nunes, C.P., 1973. Ethylene Amines. Production and Uses. *Rev. Port. Quím.* 15, 158–165.
- Huntsman, 2018, Ethylenamines - A Global Profile of Products and Services. <https://ir.huntsman.com>.
- 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.
- Maestri, F.; Rota, R., 2015, Kinetic-Free Selectivity Control of Chemical Reactions leading to Non Volatile Products. *Chem. Eng. Sci.*, 734, 108-120.
- Maestri, F.; Sacco, F.; Pirola, C; Rota, R., 2018, Selective synthesis of polyamines in multipurpose plants. *Chem. Eng. Sci.*, in press. (DOI: 10.1016/j.ces.2018.04.036).
- Steinbach, J., 1999, *Safety Assessment for Chemical Processes*; Wiley-VCH: Weinheim.
- Steensma, M., Westerterp, K.R., 1988. Thermally safe operation of a cooled semibatch reactor. Slow liquid–liquid reactions. *Chem. Eng. Sci.* 43, 2125–2132.
- Steensma, M., Westerterp, K.R., 1990. Thermally safe operation of asemibatch reactor for liquid–liquid reactions. *Slow reactions. Ind. Eng. Chem. Res.* 29, 1259–1270.
- Stoessel, F., 1993, What is your Thermal Risk? *Chem. Eng. Prog.* 68.