Selective synthesis of polyamines in multipurpose plants

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HIGHLIGHTS

- SBRR allows increasing process selectivity and plant productivity with respect to SBR.
- SBRR plant configuration can be easily assembled in every multipurpose plant.
- Experiments proved that SBRR increases performances for DCE/EDA industrial process.

GRAPHICAL ABSTRACT
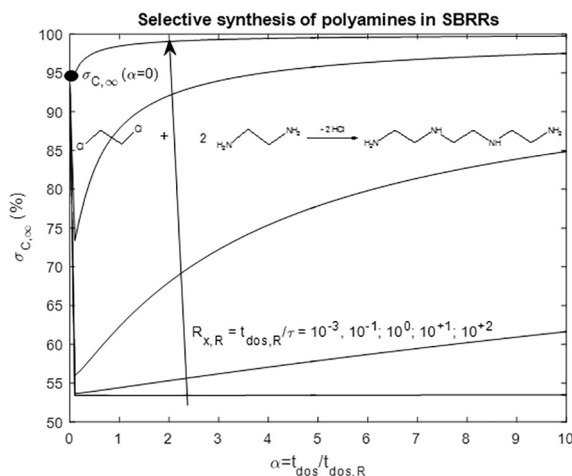
ABSTRACT

A number of reaction processes undergo yield drops since an intermediate target species can further react with one of the reactants generating lower volatility by-products. Such reactions are typically fast and non-selective, so that a gradual conversion of the reactants is recommended because of safety and quality constraints; when dealing with relatively low-volumes of a highly fragmented set of products, a semibatch reactor is normally adopted where the reaction selectivity is increased by increasing the excess of the selective reactant, therefore lowering the plant productivity.

For increasing the process selectivity without reducing the plant productivity a different reactor configuration has been recently proposed: the so-called semibatch recycle reactor. However, the good performance of this configuration has never been experimentally confirmed.

In this work, the unselective industrial synthesis of polyamines through alkylation of 1,2-dichloroethane with a diamine has been experimentally investigated both in a standard semibatch reactor as well as in a semibatch recycle reactor, showing that the latter can lead to a significant increase of both the process selectivity and productivity.

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1. Introduction

In the fine chemical as well as in the intermediates chemical industry a wide range of products of the same class are often manufactured on a campaign basis, so that multipurpose batch

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Nomenclature

Bis-AEP	N,N′-bis-(2-aminoethyl) 1,4-piperazine
C	molar concentration, kmol/m^3
DCE	1,2-dichloroethane
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
EBP	ethylenebis 1,4-piperazine
EDA	ethylenediamine
Ex	$= n_{B0,r}/n_{A1}$ or $= n_{EDA}/(2 \cdot n_{DCE})$, effective excess number, –
k	reaction rate constant, m^3/(kmol·s)
n	number of moles, kmol
n	additional monomer units to TETA or EBP (in Eqs. (14), (15) and in Fig. 4), –
n,m,p,q	reaction orders, –
PEE	poly-(ethyl-ethylenediamine)
PEEDA	N-[(2-aminoethyl) 2-aminoethyl] 1,4-piperazine
PEHA	pentaethylene-hexamine
PEP	poly-(ethylene-1,4-piperazine)
Q	reflux rate, (m^3/s)
r	DCE/EDA molar ratio in Eqs. (14) and (15), (–)
R	gas constant = 8.314, kJ/(kmol·K)
R$_x$	$= t_{dos}/\tau$, recycle number, –
t	time, s
T	temperature, K
TETA	triethylenetetramine
V	volume, m^3

Subscripts and superscripts

A,B,C,D	components A, B, C and D
c	growth with cyclization
DCE	1,2-dichloroethane
dos	dosing stream or dosing time
imp	impurity
r	reactor
R	reference
s	simple growth
TETA	triethylenetetramine
x	in the recycle number R$_x$
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	$= t_{dos}/t_{dos,R}$, –
γ	dimensionless concentration, –
ϑ	$= t/t_{dos}$, dimensionless time, –
κ	$= k/k_R$, dimensionless reaction rate constant, –
ν	DCE/byproduct molar ratio, –
σ	$= n_C/(n_{B0} - n_B)$, molar selectivity, –
τ	$= V_r/Q$, average residence time in the reactor, s
χ	$= (n_{B0} - n_B)/n_{A1}$, normalized conversion, –

or semibatch reactors are adopted instead of continuous ones (Dimian et al., 2014).

In a number of such processes the target reaction product can unselectively react with one of the reactants, generating undesired by-products (Westerterp et al., 1984), which must be then separated from the target one and finally disposed as a waste.

A number of such reactions can be found even in the intermediates chemical industry (Arpe, 2010; Garner and Nunes, 1973): as a relevant example the production of polyamines from 1,2-dichloroethane (DCE) and diamines is discussed in this work.

Polyamines have many industrial uses, ranging from the curing of epoxy resins, to the production of functionalized polyamides and chelating agents (Garner and Nunes, 1973). Moreover, polyamines are a valuable backbone for the synthesis of a number of fine chemical additives.

Starting from several diamines, the range of polyamines which can be generated for specialized applications is relatively wide, so that they are often produced in non-continuous multipurpose SBRs, in which DCE (that is, the non-selective reactant) is gradually added to a diamine excess, to control both the reaction heat and the potential gas or vapor evolution (Steinbach, 1999; Maestri and Rota, 2016; Copelli et al., 2010).

The selectivity of such processes is often limited since DCE can further react with the target bis-aminoalkyl ethylenediamine to generate heavier derivatives, which affect the process yield and the purity of the final product when they are not separated from it.

In such cases, when performing the reaction in a standard SBR, a huge excess of the diamine must be adopted in order to keep the process selectivity at acceptable values: however, such process conditions lower the plant productivity, also because of the subsequent separation of the diamine excess.

Moreover, in some cases such a separation is cumbersome through conventional distillation because of both a relatively low volatility difference between the components to be separated, and a potential azeotropic behavior of the mixture (Hiraga et al., 1986). This calls for more sophisticated separation techniques, with a significant increase of the production costs.

Whereas for some applications the raw polyamine can be used without relevant drawbacks, there are systems in which a higher purity of the product is required: for the sake of example, when high molecular weight polyamides must be generated through reaction of the polyamine with a bifunctional acid, the stoichiometric ratio between the two reactants is a key parameter, which can be guaranteed only starting from relatively pure species (Garner and Nunes, 1973).

To overcome the selectivity problem or when the required diamine is difficult to be found on the market, alternative synthesis routes are adopted: for the sake of example, N,N′-bis-(3-aminopropyl)-ethylenediamine is industrially produced through Michael addition of acrylonitrile to ethylenediamine, followed by catalytic hydrogenation of the intermediate bis-cyanoethyl derivative (Häussling et al., 1998). However, the process involves two reaction steps, one of which (that is, the hydrogenation) requires a technology not always readily available.

When producing polyamines through direct alkylation of DCE with a relatively volatile diamine, the process selectivity and productivity can be increased even in a non-continuous reaction system adopting the semi batch recycle reactor (SBRR) process (Maestri and Rota, 2013 and 2015). In such a plant configuration the diamine is refluxed through the system and the DCE dosing is spread over a suitable time period, in order to minimize the target product accumulation in the reactor. The resulting segregation between the target product and the non-selective reactant allows for effectively limiting the extent of the further alkylation of the target polyamine by DCE and hence for achieving a high process selectivity, even adopting a limited initial excess of the starting diamine.

In this work, the selectivity behavior of the reaction between 1,2-dichloroethane (DCE) and ethylenediamine (EDA) to produce triethylenetetramine (TETA) has been experimentally tested in a standard SBR and in a SBRR, in which DCE is dosed in refluxing EDA.