

The addition to TETA and EBP (as mother species) of n further monomer units of the types respectively represented in Table 2 leads to heavier derivatives, for which the DCE/EDA ratio is equal to:

$$\Gamma_{\text{DCE/EDA},s} = \frac{1+n}{2+n} \quad (14)$$

$$\Gamma_{\text{DCE/EDA},c} = \frac{3+2n}{2+n} \quad (15)$$

where the labels s and c stay for simple growth or growth with cyclization.

In Figure 4, the trends of $\Gamma_{\text{DCE/EDA},s}$ and $\Gamma_{\text{DCE/EDA},c}$ are represented. It can be noticed that, with an initial DCE/EDA ratio equal to 1:2 for TETA and 3:2 for EBP, asymptotic ratios equal to 1:1 and 2:1 are reached for simple and cyclic growth respectively, with a maximum range of variation going from 2:3 to 2:1 at $n=1$.

When performing the reaction in a standard SBR, polyaddition reactions are more likely to occur because of the theoretically infinite residence time in the reactor. Therefore, heavier byproducts (cyclic or not) of the type represented in Table 2 should be expected.

Instead, in a SBRR operated at low residence times in the top reactor (when compared to the coreactant dosing time), the original TETA undergoes most probably single additions (either intermolecular or intramolecular), generating the different species represented in Table 2.

As a consequence, for the SBRR reaction runs a DCE/EDA molar ratio ranging from 2:3 to 1:1 is expected, whereas for the SBR experiments such a ratio can vary from 1:1 to 2:1.

More in detail, for the SBR process configuration two asymptotic situations can be figured out: the first one where the impurities consist only in not cyclic polyamines with a DCE/EDA ratio at the

limit equal to 1:1, and the second one where the impurities consist of a poly-(ethylene 1,4-piperazine), with an asymptotic DCE/EDA ratio equal to 3:2.

For the SBRR process configuration, instead, the two following asymptotic situations are more likely to occur, both corresponding to a single addition to TETA: the first one where a single DCE equivalent further reacts with TETA and EDA to yield penta-ethylene hexamine, with a DCE/EDA ratio equal to 2:3, and the second one according to which DCE undergoes an internal condensation with TETA, generating monopiperazinic derivatives with a DCE/EDA ratio equal to 1.

In all the aforementioned cases, the lower the DCE/EDA ratio in the impurities is, the higher the final process selectivity is, since a higher DCE amount is available to generate the target product.

On this basis, for each SBR and SBRR experimental run a range of variation for the selectivity to TETA can be estimated (from Equation 9 through some algebra), as follows:

$$\sigma_{\text{TETA},\infty} = \frac{100}{1 + v \left(\frac{100}{\% \text{ wt TETA}} - 1 \right) \frac{M_{w,\text{TETA}}}{M_{w,\text{imp.}}}} \quad (16)$$

where v is a coefficient accounting for the molar amount of DCE per mole of impurity, $M_{w,\text{imp.}}$ is the molecular weight of the impurity, % wt. TETA is the TETA weight percent in the final reaction mixture and $M_{w,\text{TETA}}=146.24\text{g/mol}$ is the molecular weight of TETA.

This relation, for a given experimental value of % wt. TETA in the final sample, allows for estimating an asymptotic lower and upper limit of the process selectivity by introducing the $M_{w,\text{imp.}}$ and v values characterizing the by-products listed in Table 2.

In Figure 5, the expected selectivity ranges for the SBR and SBRR reaction runs are plotted as a function of the TETA assay for the limiting impurities summarized in Table 2 with respect to the two process configurations. It can be noticed that, as expected, the gap between the lower and upper selectivity values decreases when increasing the TETA assay.

In Figure 3 (as well as in the Supplementary Material Section) the experimental selectivity values measured in the SBR and SBRR runs are compared with the lower and upper selectivity limits

estimated through Equation 16. It can be noticed that in all the cases the experimental selectivity resulted to be in the estimated range.

In particular, the experimental selectivity values for the SBR runs are closer to their expected upper limits than those for the SBRR runs. Such a result suggests that even with a theoretically infinite residence time in the reactor, the generation of impurities with a DCE/EDA ratio close to the top 2:1 value (corresponding to poly-ethylene-piperazinic structures of theoretically infinite length) is less realistic. In the SBRR runs, instead, a selectivity value closer to an expected average value has been achieved, hence confirming that the real impurity pattern is reasonably close in terms of DCE/EDA ratio to that of the monoaddition byproducts reported in Table 2.

Finally, as can be noticed from Figure 3, in the operating conditions investigated for the SBRR runs, a nearly constant selectivity to TETA has been found, which confirms that the corresponding recycle numbers are always above the threshold value for an effective removal of the target product from the reactor: such a general behavior of SBRRs is expected from Figure 2 at relatively high values of the α parameter.

5. Conclusions

A number of potential runaway reaction processes performed in non-continuous plants undergo selectivity drops because of the undesired reaction of one reactant with the intermediate target product.

In these cases, when a relatively high volatility gap exists between the selective reactant and the target product, a combined selectivity and productivity increase can be achieved through the SBRR process configuration, which can be easily assembled with the equipment available in any multipurpose plant (Maestri and Rota, 2013 and 2015).

In this work the selectivity behavior of the SBRR process configuration vs. a standard SBR one has been experimentally investigated through a case-study of industrial relevance, that is, the alkylation of ethylenediamine through 1,2-dichloroethane to produce triethylenetetramine.

Adopting the SBRR process configuration a relevant increase of both the process selectivity and productivity has been achieved, generating yet in the reaction step a product of higher purity than that available on the market.

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 Equations 14, 15 and in Figure 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 Equations 14 and 15, (-)
R	gas constant = 8.314, kJ/(kmol·K)
R _x	= t_{dos}/τ , 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	= $t_{dos}/t_{dos,R}$, -
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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, -

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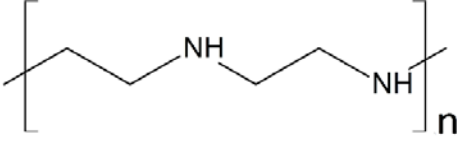
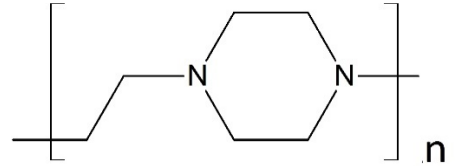
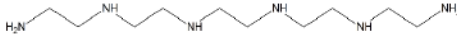
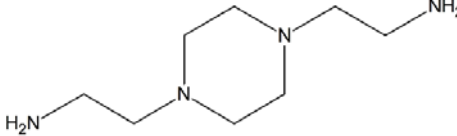
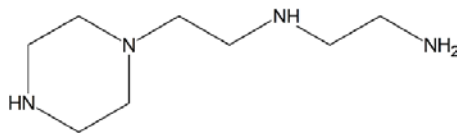
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Tables

Table 1: Operating conditions of the SBR and SBRR runs, carried out at 50°C.

Run	Ex number	R_x number
SBR1	5.91	0
SBR2	5.43	0
SBR3	5.46	0
SBR4	5.51	0
SBR5	5.44	0
SBRR1	0.65	20
SBRR2	0.65	24
SBRR3	0.67	38
SBRR4	0.65	54
SBRR5	0.65	101
SBRR6	0.65	115
SBRR7	0.65	141
SBRR8	0.65	172
SBRR9	0.65	237
SBRR10	0.92	239

Table 2: Expected classes of TETA impurities with respect to the DCE/EDA ratio for SBR and SBRR runs.

Chemical name	Chemical formula	Molecular weight	DCE/ED A ratio	Process conditions
Poly-(ethyl-ethylenediamine) (PEE)		$(86)_n$ g/mol	1:1	SBR
Poly-(ethylene-1,4-piperazine) (PEP)		$(112)_n$ g/mol	2:1	SBR
Pentaethylene-hexamine (Linear-PEHA)		232 g/mol	2:3	SBRR
N,N'-bis-(2-aminoethyl) 1,4-piperazine (Bis-AEP)		172 g/mol	1:1	SBRR
N-[(2-aminoethyl) 2-aminoethyl] 1,4-piperazine (PEEDA)		172 g/mol	1:1	SBRR

Captions to the figures

Fig. 1.

SBRR process configuration for the selective synthesis of triethylenetetramine.

Fig. 2.

SBRR process configuration. $\gamma_1=\gamma_2=30$; $n=m=p=q=1$; $T/T_R=1.1$; $Da_1=Da_2=1$ at $t_{dos}=t_{dos,R}$. Final selectivity to C vs. dimensionless dosing time for $Ex=2$ (A) and $Ex=1$ (B).

Fig. 3.

Selective synthesis of triethylenetetramine. Experimental selectivity vs. recycle number. (o) Experimental values. (I) Estimated range of selectivity values based on the expected by-products.

Fig. 4.

DCE/EDA molar ratio in the expected byproducts vs. equivalents of further reacted EDA.

Fig. 5.

Expected selectivity ranges vs. final TETA assay for the SBR and SBRR process configurations. Comparison with the experimental results for the SBR (^) and SBRR (o) reaction runs.

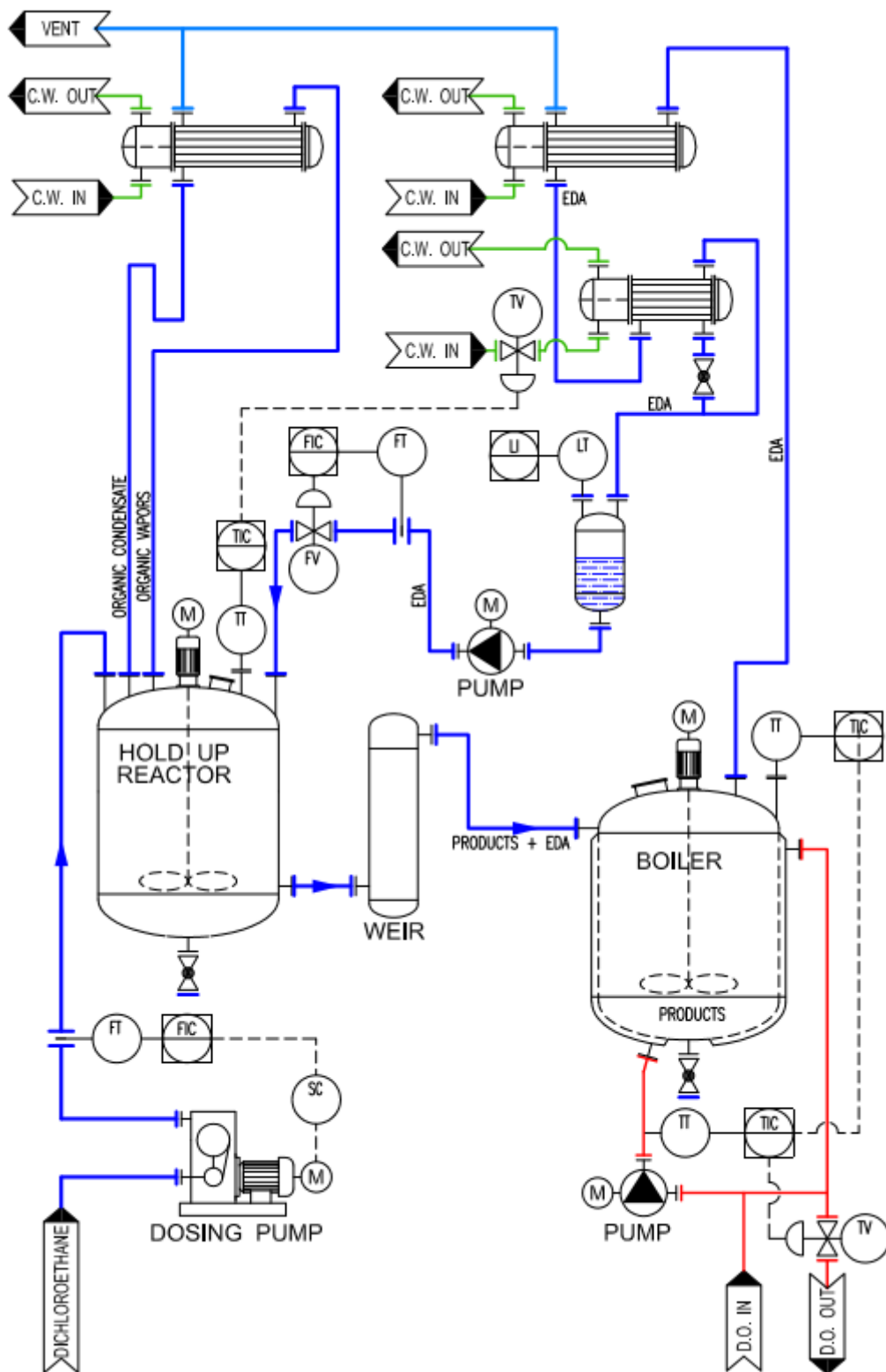


Fig.1

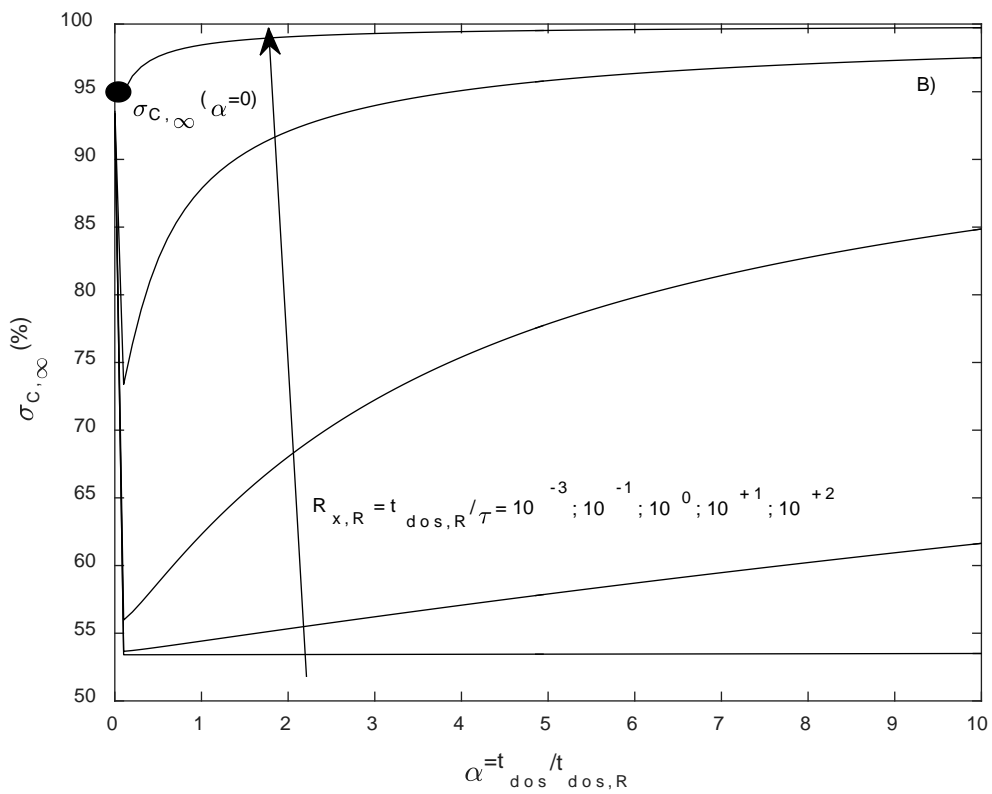
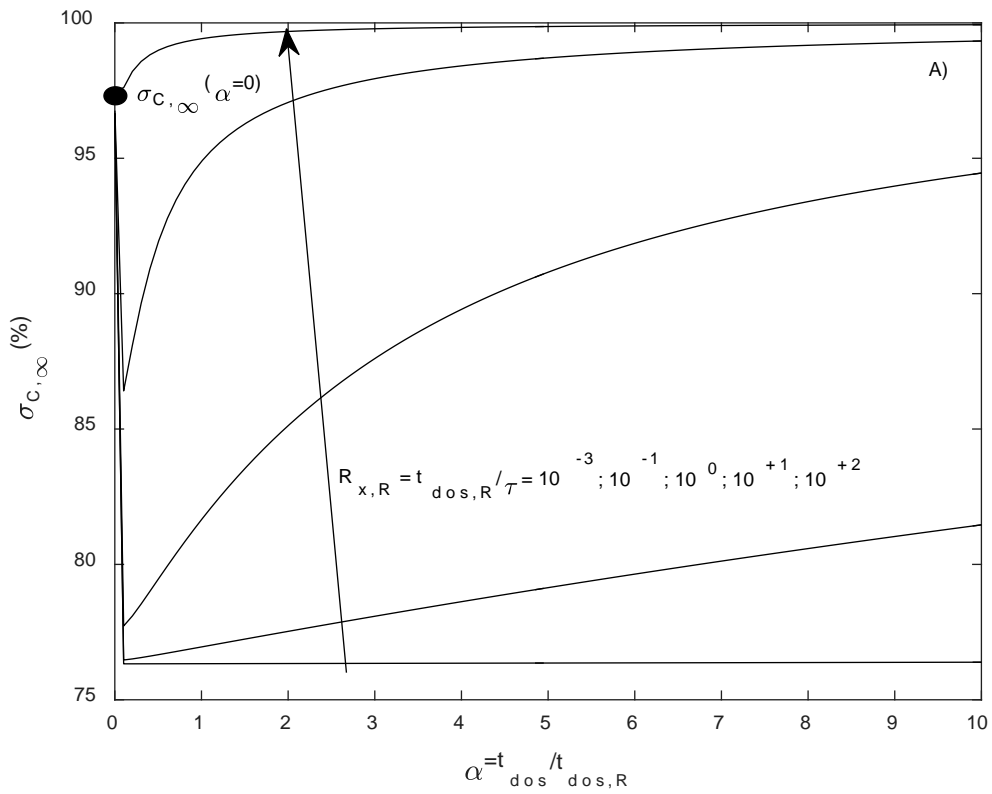


Fig. 2

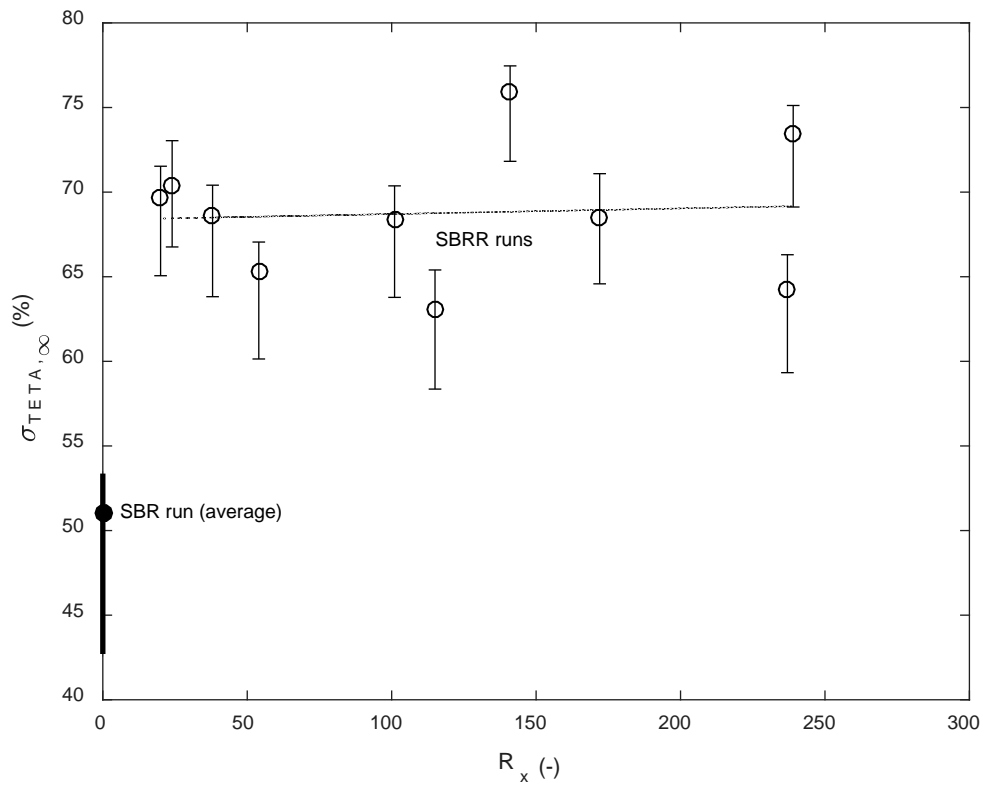


Fig. 3

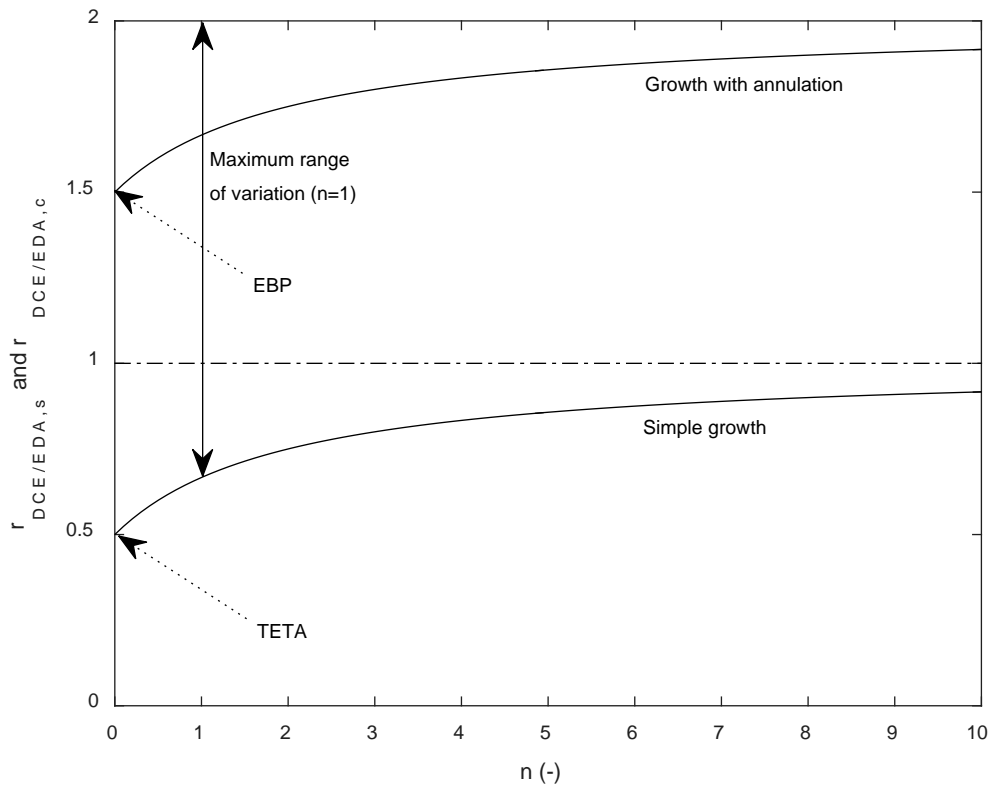


Fig. 4

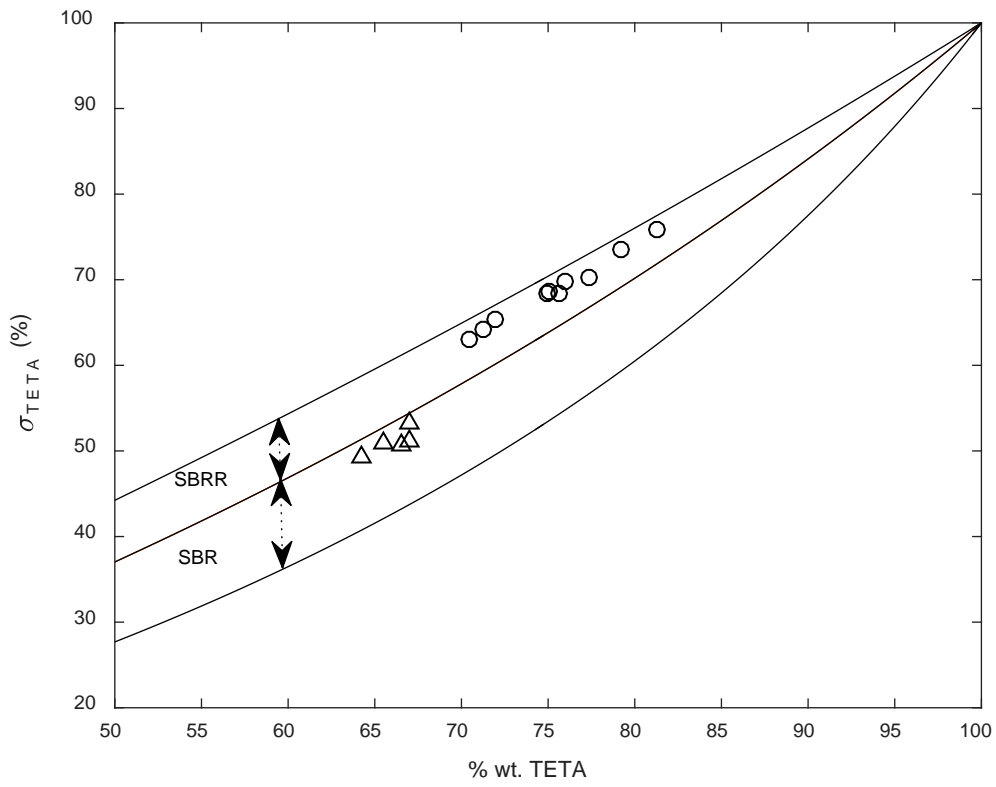


Fig. 5