

Analysis of reactor–separator processes for polymeric and oligomeric degradation products with controlled molar mass distributions

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21 **Abstract**

22 Integration of reaction and separation is attractive in production of biobased oligomers and short
23 polymers from polysaccharides and proteins via catalytic degradation. The challenge lies in
24 controlling the molar mass distribution. Theoretical analysis for process integration is performed
25 for conventional CSTR, a multifunctional reactor, and reactor-separator-recycle processes.
26 Closed-form solutions for the mass balance equations are obtained for coupled serial-parallel
27 first-order reactions. The influence of the separators' cut-off range and sharpness on the feasible
28 operating parameter range and process performance is visualized. It is found that a membrane
29 reactor may be less productive than a CSTR if total concentration is limited. An additional
30 separator to recycle the solvent significantly improves purity and productivity. Solvent recycling
31 decouples the feed rate and the residence time of the product molecules. To maximize purity and
32 productivity, no product molecules should be retained in the reactor whereas the recycled solvent
33 can be impure.

34

35 **Keywords**

36 Reactor-separator; membrane reactor; process intensification; depolymerization; polysaccharide;
37 protein

38

39 **1. Introduction**

40 A major approach to improve the efficiency of chemical processes is the integration of reaction
41 and separation operations [1]. The most frequent motivations for this are that continuous or
42 periodic removal of products from the reaction locus and/or recycling of unused reactants may
43 increase the conversion for equilibrium limited reversible reactions and improve selectivity and
44 yield for multistep reaction systems [2–4].

45 Generally, there exist two main approaches for integrating reaction and separation. The first
46 approach are multifunctional reactors where the separation is performed directly inside the
47 reactor vessel. Examples for such processes, which are also denoted as fully-integrated reactor-
48 separators or as reactive separations, are known as reactive distillation, reactive extraction,
49 reactive chromatography, etc.. For an overview on corresponding approaches see [5] and [6].
50 While the use of multifunctional reactors can be attractive regarding equipment costs, they are
51 suitable only if there exists a common “window of operation” for reaction and separation, *i.e.*,
52 both can be carried out under same operating conditions and involved mass transfer operations
53 are not significantly slower than the reaction [7],[8]. In the second approach, recycle-integrated
54 reactor-separators, either the effluent or a side stream from the reactor is treated in an external
55 separator to produce a product stream, while one or more streams are sent back to the reactor. In
56 comparison to multifunctional reactors, this allows for more degrees of freedom to optimize each
57 unit operation, but at the expense of higher equipment costs.

58 Reactor-separator systems pose several challenges regarding design, dynamic behavior and
59 stability, and control. For the choice of the best reactor-separator concept and its optimal design,
60 systematic approaches have been proposed for network construction [9] and optimization of
61 process superstructures by mixed integer nonlinear programming [10], [11] or generalized
62 disjunctive programming [12]. Furthermore, reactor-separator processes can exhibit peculiar
63 nonlinear dynamics (in particular if they include recycle streams), including multiple steady
64 states, oscillations, and runaways [13]. Their behavior may crucially depend on the mode of
65 operation (see, e.g. [14]), which requires careful analysis of the configuration at hand. However,
66 stability analysis of reactor-separators is rather well developed and recycle streams may even
67 allow for simplifying the control tasks. For example, Kiss et al. [15] have shown that strongly
68 non-linear processes are better controlled via the recycle stream rather than via the feed stream.

69 It is noteworthy that most theoretical studies analyzing reactor-separators are concerned with
70 relatively small molecules and include only a small number of chemical species. In practical
71 studies, however, reactor-separators are often used for complex raw materials in biorefining and
72 food technology applications, where mixtures contain a multitude of similar, molar weight-
73 distributed components. For example, galacto-oligosaccharides have been synthesized by
74 enzymatic polymerization from lactose and dairy side streams containing lactose using
75 membrane reactors [16] [17]. Another typical application is the production of smaller molecules
76 with high added value via degradation of biopolymers. Examples in dairy industries include the
77 production of bioactive peptides. Pepsin was used to produce α -lactorphin from goat whey in a
78 continuous ultrafiltration membrane reactor [18]. Enzymatic degradation of casein
79 glycomacropptide to 3'-sialyllactose was studied in a simple dead-end batch membrane reactor
80 [19]. In a more advanced process, two continuous reactor-separator-recycle units were connected
81 in series to hydrolyze casein [20]. In the first unit, an endopeptidase was used to produce a
82 hydrolysate with antioxidant properties and, in the second unit, an exopeptidase was used to
83 reduce its bitter taste. As to biorefining, plant polysaccharides depolymerized in membrane
84 reactors include cellulose [21], [22], hemicelluloses such as Konjac glucomannan [23], and
85 chitosan [24]. For more details on enzyme membrane reactors for production of
86 oligosaccharides, see recent reviewed by Su et al. [25]. A reactor-separator-recycle process
87 where the hydrolysis of inulin is carried out in a tubular reactor using an immobilized enzyme
88 has been studied numerically [26].

89

90 Summarizing, practical realizations of the challenging synthesis problems above already rely on
91 advanced reactor-separator processes like multifunctional membrane reactors. Also powerful
92 tools are available for detailed system analysis and optimal design, especially for smaller
93 molecules. However, there is a lack of fundamental studies regarding the potential of the
94 different reactor-separator concepts for processing complex, molar mass-distributed products
95 from synthesis and degradation reactions.

96 Therefore, this study analyses and compares different reactor-separator systems for the
97 continuous production of oligomers and short polymers by depolymerization of macromolecules
98 and degradation of short oligomers. The processes considered cover both multifunctional
99 reactors and different reactor-separator-recycle processes. Along this, a process with independent
100 recycles for unreacted reactant and solvent is proposed as an improvement for such applications.

101 Based on a reaction mechanism for first-order isothermal series-parallel degradation reactions
 102 and corresponding material balances, explicit steady-state solutions are derived for the different
 103 processes. Feasible regions of the operating parameters (space-time, solvent recycling rate) are
 104 visualized and the effect of separator characteristics (sharp, nonsharp) on productivity and purity
 105 are analyzed. The practical problem of selecting the cut-off size of the separator relative to the
 106 desired molar mass distribution of products is also addressed.

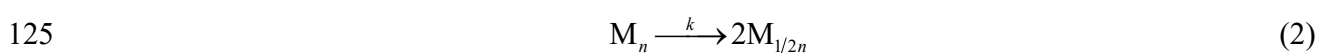
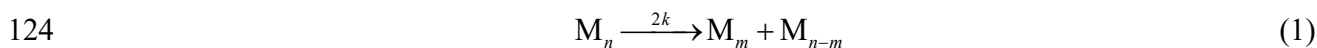
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108 2. Theory and calculations

109 2.1 Reaction schemes

110 Cleavage of the bonds in biopolymers has been catalyzed with mineral acids and organic acids
 111 [27] [28], ion exchange fibers and resins [29,30], gamma irradiation [23] as well as soluble or
 112 immobilized enzymes [25]. Here the random scission mechanism [31] is considered for
 113 simplicity, but no assumptions are made regarding the catalyst type. All molecules are regarded
 114 as linear homopolymers. The probability of cleavage of each bond in a molecule is equal and
 115 independent of the degree of polymerization. Degradation of monomers is not considered.
 116 Extension to more complex polymers, mixtures of polymers, as well as more complex
 117 degradation reaction schemes [30] [32], is straightforward using numerical methods and is not
 118 discussed.

119 In the present reaction scheme, a polymer M_n with degree of polymerization n breaks into lower
 120 polymers M_m and M_{n-m} as in Eq. (1). There are $(n-1)/2$ such parallel reactions if n is odd and
 121 $n/2-1$ parallel reactions if n is even. A special case is cleavage of the middle bond in molecules
 122 with n even, Eq. (2). The rate constant for reaction (1) is double that of reaction (2) because of
 123 symmetry of the molecules.

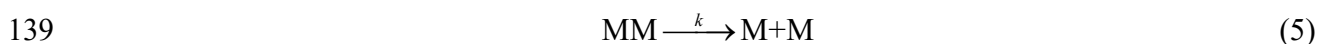
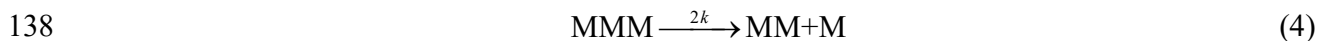


126 Each of the degradation products can break further according to a similar set of parallel
 127 reactions. This quickly leads to a very large number of mixture components and reactions. Let us
 128 assign an index $j = 1$ to the largest molecule in the system at the initial state and let j strictly
 129 increase with decreasing degree of polymerization, *i.e.* $DP(j) = N+1-j$. Molecule j is formed
 130 from each of the larger molecules in two first-order reactions because all homopolymers are
 131 symmetrical. Since each of the $N-j$ bonds in molecule j can react with equal probability, the net
 132 rate of formation for j becomes

$$133 \quad r_j = 2k \sum_{m=1}^{j-1} c_m - (N-j)kc_j \quad (3)$$

134

135 In addition to the general system described above, we will study the production of dimer MM
 136 from trimer MMM as the simplest reaction system that follows this scheme. The monomer M is
 137 an impurity. This system involves the following reactions



140

141 and the net rates of formation become

$$142 \quad r_{\text{MMM}} = -2kc_{\text{MMM}} \quad (6)$$

$$143 \quad r_{\text{MM}} = 2kc_{\text{MMM}} - kc_{\text{MM}} \quad (7)$$

$$144 \quad r_{\text{M}} = 2k(c_{\text{MMM}} + c_{\text{MM}}) \quad (8)$$

145

146 2.2 CSTR-based reactor–separator concepts

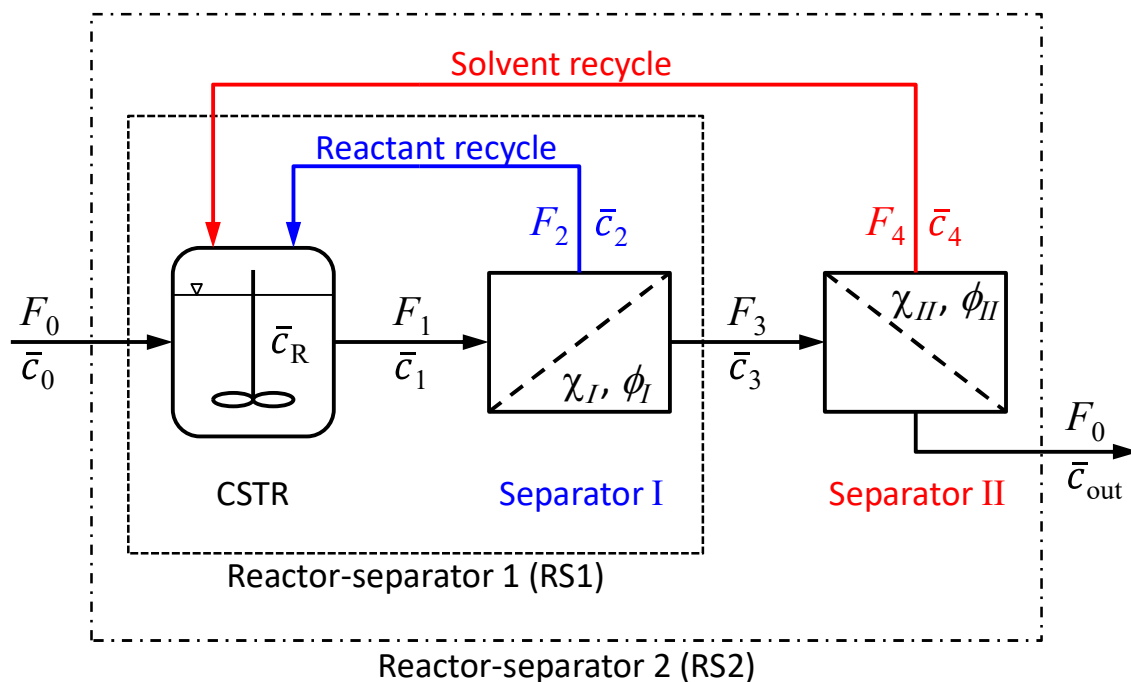
147 The different reactor–separator process options considered represent sub-sets of the
 148 superstructure in Fig. 1 that contains a reactor and two (optional) separators. The feed solution
 149 containing the (possibly polydisperse) homopolymer to be degraded into products is fed into an
 150 ideal continuous stirred tank reactor (CSTR) at volumetric flow rate F_0 and in concentrations \bar{c}_0 .
 151 Some molecules with an intermediate molar mass are regarded as the target product, whereas too
 152 small and large molecules are impurities. The degradation reactions follow the reaction
 153 mechanism described above and are assumed to occur in the reactor vessel only. Only steady
 154 state operation of the process options is considered.

155 The unreacted reactants (*i.e.*, too large molecules) can be recycled into the CSTR using Separator
 156 I, and solvent may be recycled by using Separator II. The separators are regarded as non-sharp
 157 (*i.e.*, the separation between mixture components may be incomplete), but they are considered
 158 ideal in the sense that the separation quality is independent of the flow rates and solute
 159 concentrations. Note, that we indicate the separators in Fig. 1 as membrane units, since these are
 160 a typical choice for this type of application. However, it is emphasized that our analysis holds for
 161 any type of separation unit or mechanism.

162 The different process options considered are obtained from the superstructure in Fig. 1 by simply
 163 “turning on or off” the separators and their recycles. The case of a conventional stand-alone
 164 reaction without separation (denoted below as “stand-alone CSTR”) corresponds to $F_2 = F_4 = 0$,
 165 $F_1 = F_3 = F_0$, and $\bar{c}_{\text{out}} = \bar{c}_3 = \bar{c}_1$. A reactor–separator system that consists of the CSTR and
 166 Separator I for reactant recycling is denoted by “RS1” (dashed box in Fig. 1). In this case, $F_4 = 0$,
 167 $F_3 = F_0$, and $\bar{c}_{\text{out}} = \bar{c}_3$. It should be noted that in the frame of our analysis, the reactor-separator-
 168 recycle process RS1 is fully equivalent to a multifunctional reactor-separator (for instance a
 169 membrane reactor). The third process scheme, denoted as “RS2” (dash-dotted box in Fig. 1),
 170 includes both Separator I for reactant recycling, as well as Separator II for solvent recycling.
 171 Another option could be to operate RS2 without Separator I (*i.e.*, bypassing this unit such that

172 $F_2 = 0$, $F_3 = F_1$ and $\bar{c}_3 = \bar{c}_1$). However, this case is not considered here since a mere solvent
 173 recycling would not be useful, and a typical size-dependent separation in Separator II would
 174 correspond to retaining the smaller reactants more than the products. Even if Separator II would
 175 reject larger molecules less than smaller molecules, this option would become equivalent to RS1.

176



177

178 Figure 1. A superstructure representing the considered continuous reactor–separator process
 179 schemes for degradation of large homopolymers into products with intermediate molar mass.
 180 The reaction is performed in an ideal CSTR, while the optional Separators I and II allow
 181 recycling unreacted reactants and solvent. The reactor-separator-recycle scheme RS1 is fully
 182 equivalent to a multifunctional reactor with internal retention of reactant. The complete process
 183 RS2 allows for independent adjustment of the reactant and solvent recycles.

184

185 Obviously, the two processes representing the stand-alone CSTR and the reactor-separator RS1
 186 are simply special cases of process RS2. This facilitates analyzing all processes based on the
 187 same material balance equations, as demonstrated below.

188 Let us introduce a flow splitting parameter $\phi_k = F_k^{\text{pass}} / F_k^{\text{in}}$. These are regarded as operating
 189 parameters that describe how separator k splits the incoming flow F^{in} into two streams, “pass”
 190 and “reject”. From this definition follows

$$191 \quad F_k^{\text{pass}} = \phi_k F_k^{\text{in}} \quad (9)$$

$$192 \quad F_k^{\text{reject}} = (1 - \phi_k) F_k^{\text{in}} = \frac{1 - \phi_k}{\phi_k} F_k^{\text{pass}} \quad (10)$$

193

194 In a similar manner, the ability of a solute j to pass through separator k is described with a mass
 195 splitting parameter $\chi_{k,j} = c_{k,j}^{\text{pass}} / c_{k,j}^{\text{in}}$. Using the notation in Fig. 1 for labelling the streams, the
 196 flow and mass split ratios the two separators are

$$\begin{aligned} \text{Separator I: } \phi_I &= F_3 / F_1, \quad \chi_{I,j} = c_{3,j} / c_{R,j} \\ \text{Separator II: } \phi_{II} &= F_4 / F_3, \quad \chi_{II,j} = c_{4,j} / c_{3,j} \end{aligned} \quad (11)$$

198 Note that one may as well re-formulate the above definitions; for example, using a retention
 199 factor as commonly used in membrane separations.

200 Equations for calculating the concentrations of solutes in the reactor vessel, \bar{c}_R , and in the
 201 effluent, \bar{c}_{out} , are derived as follows. In an isothermal system with constant fluid density, the
 202 effluent flow rate must equal the fresh feed flow rate F_0 . The material balance for molecule j
 203 over the entire process can thus be written as

$$F_0 c_{0,j} - F_0 c_{\text{out},j} + r_j (\bar{c}_R) V_R = 0 \quad (12)$$

205

206 Here we wish to eliminate c_{out} in Eq. (12) by writing it in terms of \bar{c}_R and the operating
 207 parameters of the two separators. The material balance over Separator II gives

$$F_0 c_{\text{out},j} = F_3 c_{3,j} - F_4 c_{4,j} \quad (13)$$

209

210 and Eq. (12) becomes

$$c_{0,j} - \frac{F_3}{F_0} c_{3,j} + \frac{F_4}{F_0} c_{4,j} + r_j (\bar{c}_R) \tau_0 = 0 \quad (14)$$

212

213 where $\tau_0 = V_R / F_0$ is the space-time of the reactor vessel without considering recycling. The flow
 214 rate ratios and the unknown concentrations c_3 and c_4 in Eq. (14) can be expressed using the
 215 operating parameters of the two separators, ϕ_I and ϕ_{II} , as

$$\frac{F_3}{F_0} = \frac{1}{1 - \phi_{II}}, \quad \frac{F_4}{F_0} = \frac{\phi_{II}}{1 - \phi_{II}} \quad (15)$$

$$c_{3,j} = \chi_{I,j} c_{R,j}, \quad c_{4,j} = \chi_{II,j} c_{3,j} = \chi_{I,j} \chi_{II,j} c_{R,j} \quad (16)$$

218

219 The material balance over the entire process hence becomes

220
$$c_{0,j} + \frac{\phi_{II} \chi_{II,j} - 1}{1 - \phi_{II}} \chi_{I,j} c_{R,j} + r_j(\bar{c}_R) \tau_0 = 0 \quad (17)$$

221

222 To analyze a multicomponent reaction mixture, it is straightforward to form a set of algebraic
 223 Eqs. (17) that are coupled through the reaction rate terms, $r_j(\bar{c}_R)$, and solve it (numerically, if
 224 needed) for the concentrations of all species in the reactor, \bar{c}_R .

225 It is noteworthy that a stepwise analytical solution is possible for irreversible serial reactions. For
 226 our current reaction scheme, Eqs. (1) and (2) **Error! Reference source not found.**, this results in
 227 Eq. (18). This set of equations is an explicit formulation when the calculations are carried out in
 228 increasing order of molecule index j .

229
$$c_{R,j} = \frac{c_{0,j} + 2k\tau_0 \sum_{m=1}^{j-1} c_{R,m}}{\frac{1 - \phi_{II} \chi_{II,j}}{1 - \phi_{II}} \chi_{I,j} + (N - j) k \tau_0} \quad (18)$$

230

231 The concentrations in the effluent of the reactor–separator process, $c_{out,j}$, are obtained from the
 232 material balance over Separator II, Eq. (13). This can be written in terms of the flow and mass
 233 split ratios as in Eq. (19). Alternatively, $c_{out,j}$ can be calculated from the global mass balance in
 234 Eq. (12).

235
$$c_{out,j} = \frac{1 - \phi_{II} \chi_{II,j}}{1 - \phi_{II}} \chi_{I,j} c_{R,j} \quad (19)$$

236

237 An important special case is an ideal system where Separator II is operated to recycle pure
 238 solvent to the reactor. This requires that $\chi_{II,j} = 0$ and $\phi_{II} \neq 0$, and Eqs. (18) and (19) reduce to

239
$$c_{R,j} = \frac{c_{0,j} + 2k\tau_0 \sum_{m=1}^{j-1} c_{R,m}}{(1 - \phi_{II})^{-1} \chi_{I,j} + (N - j) k \tau_0} \quad (20)$$

240
$$c_{out,j} = (1 - \phi_{II})^{-1} \chi_{I,j} c_{R,j} \quad (21)$$

241

242 2.3 Process performance parameters

243 The performance indicators used here to compare the reactor–separator process options are
 244 productivity, product purity, selectivity, and yield. They are defined based on masses instead of
 245 molar amounts. The molecules are numbered such that reactant molecules have consecutive

246 indices $j \in [1, p_1 - 1]$, the product molecules have indices $j \in [p_1, p_2]$, and impurities have
 247 indices $j \in [p_2 + 1, N]$.

248

249 Productivity, PR , is defined as the mass flow of target molecules in the effluent stream per
 250 reactor volume and unit time

$$251 \quad PR = \frac{M_{w,0}}{\tau_0} \sum_{j=p_1}^{p_2} c_{out,j} DP_j \quad (22)$$

252

253 where $M_{w,0}$ is the molar mass of a monomer. Purity, PU , is the mass fraction of the target
 254 molecules in the product stream, whereas selectivity, S , is calculated by considering only the
 255 smaller degradation products as impurities in the effluent.

$$256 \quad PU = \frac{\sum_{j=p_1}^{p_2} c_{out,j} DP_j}{\sum_{j=1}^N c_{out,j} DP_j} \quad (23)$$

$$257 \quad S = \frac{\sum_{j=p_1}^{p_2} c_{out,j} DP_j}{\sum_{j=p_2+1}^N c_{out,j} DP_j} \quad (24)$$

258

259 Yield, Y , is defined as the mass of products in effluent relative to the mass of reactants
 260 consumed, as shown in Eq. (25).

$$261 \quad Y = \frac{\sum_{j=p_1}^{p_2} c_{out,j} DP_j}{\sum_{j=p_1}^N c_{out,j} DP_j} = \left(1 + \frac{1}{S}\right)^{-1} \quad (25)$$

262

263 An interesting special case is complete conversion of reactants, for which $PU = Y$. This is
 264 achieved when Separator I retains all reactants in the system.

265

266 **3 Ternary system $MMM \rightarrow MM \rightarrow M$**

267 To better understand the interactions and the impact of the different units on process
 268 performance as well as to identify general trends, it is useful to first analyze the reactor–separator
 269 concepts in Fig. 1 for a simplified system of three molecules that react according to first order
 270 reactions in Eqs. (4) and (5). Concentrations in process schemes RS1 and RS2 can be calculated
 271 by using Eqs. (18) and (19), and choosing appropriate values for the flow and mass split ratios of
 272 the separators. We focus on the important case of ideal processes, where Separator I is assumed
 273 to reject MMM completely ($\chi_{I,MMM} = 0$) but gives no rejection for MM and M ($\chi_{I,MM} = \chi_{I,M} = 1$).
 274 In RS1, there is no solvent recycling and $\phi_{II} = 0$. In RS2, Separator II rejects all solutes but lets
 275 the solvent pass through ($\phi_{II} = 1$).

276 The equations derived in Section 2.2 apply also for the stand-alone CSTR by assuming that all
 277 solutes and the solvent pass Separator I ($\chi_{I,j} = 1$, $\phi_I = 1$) but are rejected in Separator II ($\chi_{II,j} = 0$,
 278 $\phi_{II} = 0$).

279 The explicit equations resulting for the concentrations of MMM, MM and M in each of these
 280 three reactors are given in Table 1 together with the expressions for the performance parameters.
 281 Note that $c_{out,MMM} = 0$ in both RS1 and RS2. In RS1, the outlet concentrations of MM and M
 282 equal those in the reactor whereas in the RS2 they are calculated from Eq. (21).

283

284 The conversion reached for reactant MMM in the case of a stand-alone CSTR is calculated in the
 285 usual manner (Eq. (29) in Table 1). Large values of $k\tau_0$ are required to achieve high conversions.
 286 For example, with $k\tau_0 = 1$, the CSTR yields 67% conversion, whereas 95% conversion requires
 287 $k\tau_0 = 9.5$. Conversion of MMM in the considered ideal reactor–separators RS1 and RS2 is,
 288 however, always 100% owing to the assumed perfect separation by Separator I. It is therefore
 289 more meaningful to analyze and compare these reactor concepts in terms of the purity of MM in
 290 the effluent and the productivity of the process instead of conversion.

291 Productivity is calculated using Eq. (30) in Table 1 and its dependency on $k\tau_0$ is illustrated for a
 292 generic case on the left in Fig. 2. High productivity in the CSTR is possible only with a low
 293 value of $k\tau_0$, which means, on the other hand, that a lot of unreacted MMM is lost because of also
 294 low conversion. Both RS1 and RS2 yield higher productivity than the stand-alone CSTR,
 295 especially at low space-time values. It is noteworthy that recycling the solvent in RS2 increases
 296 productivity. The upper limit for productivity in RS2 is independent of the reaction rate,
 297 $PR = M_{w,MM} c_{0,MMM} / \tau_0$, and is achieved with infinite recycle flow relative to fresh feed ($\phi_{II} = 1$).

298

299 Table 1. Equations for the performance of a stand-alone CSTR and the reactor-separator
 300 processes RS1 and RS2 for the ternary reaction system in Eqs. (4) and (5). Assumptions: fresh
 301 feed contains only MMM; MMM is completely rejected by Separator I whereas MM and M pass
 302 through; all solutes are completely rejected by Separator II.

| stand-alone CSTR | RS1 | RS2 | Eq. |
|---------------------|-----|-----|-----|
|---------------------|-----|-----|-----|

$$\frac{c_{R,MMM}}{c_{0,MMM}} = \frac{1}{1+2k\tau_0} \quad \frac{1}{2k\tau_0} \quad \frac{1}{2k\tau_0} \quad (26)$$

$$\frac{c_{R,MM}}{c_{0,MMM}} = \frac{2k\tau_0}{(1+k\tau_0)(1+2k\tau_0)} \quad \frac{1}{1+k\tau_0} \quad \frac{1}{(1-\phi_{II})^{-1}+k\tau_0} \quad (27)$$

$$\frac{c_{R,M}}{c_{0,MMM}} = \frac{2k\tau_0}{1+2k\tau_0} \left(1 + \frac{2k\tau_0}{1+k\tau_0} \right) \quad 1 + \frac{2k\tau_0}{1+k\tau_0} \quad (1-\phi_{II}) \left(1 + \frac{2k\tau_0}{(1-\phi_{II})^{-1}+k\tau_0} \right) \quad (28)$$

$$X_{MMM} = 1 - (1+2k\tau_0)^{-1} \quad 1 \quad 1 \quad (29)$$

$$PR_{MM} = \frac{4kM_{w,0}c_{0,MMM}}{(1+k\tau_0)(1+2k\tau_0)} \quad \frac{2kM_{w,0}c_{0,MMM}}{k\tau_0+k^2\tau_0^2} \quad \frac{2kM_{w,0}c_{0,MMM}}{k\tau_0+(1-\phi_{II})k^2\tau_0^2} \quad (30)$$

$$\beta = 1 \quad \frac{1+2k\tau_0}{2k\tau_0} \quad \frac{(1+k\tau_0)(1+2k\tau_0)}{2k\tau_0(1+(1-\phi_{II})k\tau_0)} \quad (31)$$

$$PU_{MM} = \frac{1}{\frac{7}{4}+2k\tau_0+\frac{3}{4}\frac{1}{k\tau_0}} \quad \frac{2}{3}\frac{1}{1+k\tau_0} \quad \frac{2}{3}\frac{1}{1+(1-\phi_{II})k\tau_0} \quad (32)$$

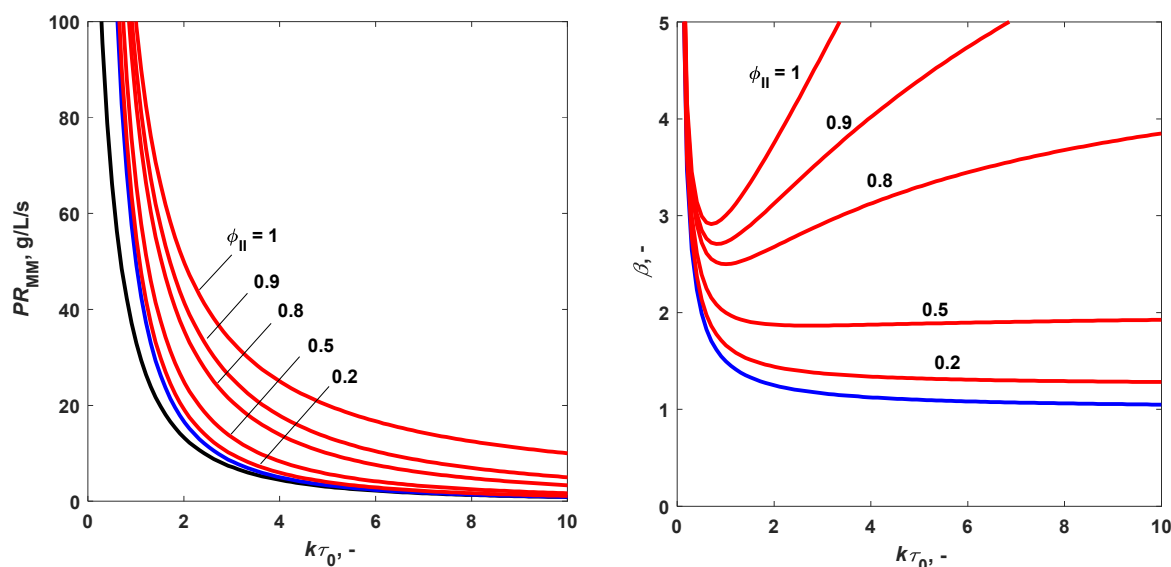
$$Y_{MM} = \frac{2}{3}\frac{1}{1+k\tau_0} \quad \frac{2}{3}\frac{1}{1+k\tau_0} \quad \frac{2}{3}\frac{1}{1+(1-\phi_{II})k\tau_0} \quad (33)$$

$$S_{MM} = \frac{2}{1+3k\tau_0} \quad \frac{2}{1+3k\tau_0} \quad \frac{2}{1+(3-\phi_{II})k\tau_0} \quad (34)$$

303

304 The difference between the two reactor–separators is highlighted by using the stand-alone CSTR
 305 as a reference and calculating the productivity ratios $\beta = PR_{RS}/PR_{CSTR}$. These are given by Eqs.
 306 (31) and presented on the right in Fig. 2. While the RS1 quickly loses its benefit relative to the
 307 CSTR when $k\tau_0$ increases, recycling the solvent in RS2 increases productivity relative to CSTR
 308 strongly at higher space-time values. The cause of this is that solvent recycling allows to
 309 decouple the mass flow of MMM into the reactor and the mean residence time of MM and M in
 310 the process. Increasing ϕ_{II} in RS2 decreases the residence time of MM in the reactor, and thus
 311 reduces its degradation to M, without affecting the residence time of MMM (which is infinite
 312 because $\chi_{1,MMM} = 0$). Such decoupling of reactant feed rate and product removal rate is not
 313 possible in the stand-alone CSTR or in RS1. Note that a value of $\phi_{II} = 0.80$ corresponds to $F_4 =$
 314 $4F_0$ according to Eq. (10). This shows that relatively large recycle flows in RS2 are required to
 315 improve PR significantly.

316

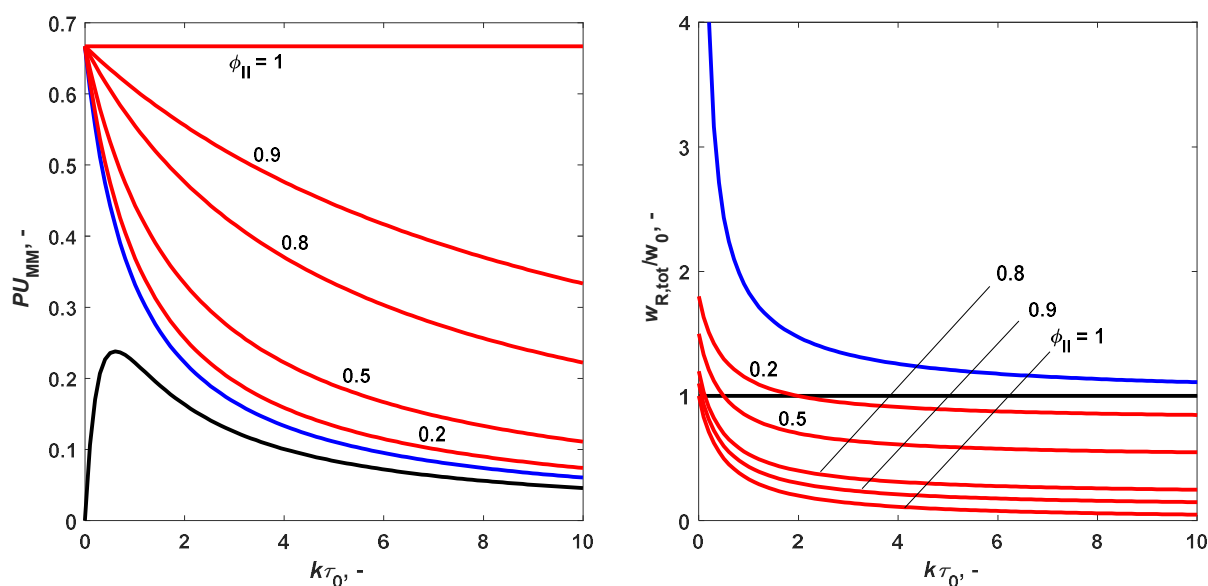


317 Figure 2. Performance of stand-alone CSTR (black) vs. that of the ideal reactor-separators RS1
 318 (blue), and RS2 (red) for the production of target component MM in the ternary reaction system
 319 as function of the flow splitting ratios in the separators. β denotes the productivity of RS1 (blue)
 320 and RS2 (red) relative to that of the stand-alone CSTR. Parameter values: $M_0 = 50$ g/mol, $c_{0,MMM} = 1$
 321 mol/L, $k = 1$ s⁻¹. Operating parameters in RS1: $\chi_{I,MMM} = 0$; $\chi_{I,MM} = \chi_{I,M} = 1$; $\phi_{II} = 0$. Operating
 322 parameters in RS2: $\chi_{I,MMM} = 0$; $\chi_{I,MM} = \chi_{I,M} = 1$; $\chi_{II,MM} = \chi_{II,M} = 0$.

323
 324 The benefit of the reactor-separators over the CSTR is seen also in the purity of the target
 325 component MM in the outlet. Purities (as weight fraction) can be calculated explicitly by using
 326 Eqs. (32) in Table 1 and are shown in Fig 3. As expected, there is a local maximum in PU_{MM} for
 327 the stand-alone CSTR with serial reaction systems. Low space-time leads to low conversion of
 328 MMM and long space-time to degradation of MM. As MMM is completely rejected by Separator
 329 I, purity and yield are interchangeable for the reactor-separators. As to RS2, low space-time and
 330 high recycle ratios are beneficial. The upper limit $PU_{MM} = 2/3$ at $\phi_{II} = 1$ corresponds to the
 331 stoichiometry of the degradation of MMM (weighted with molar masses). This is because an
 332 infinite recycle flow rate removes all MM from the reactor before it is degraded to M.

333
 334 Interestingly, Eqs. (18) to (21) and those in Table 1 show that the flow split ratio ϕ_1 of Separator I
 335 does not affect the performance of RS1 and RS2. This is because the residence times of MM and
 336 M in the reactor vessel do not depend on F_1 and F_2 but on F_3 . Since $\phi_1 = 1 - F_2/F_1$ (see Eq. (10)),
 337 ϕ_1 cannot have an effect on the solute residence times. To affect the residence times by changing
 338 F_3 , one must change also F_4 because the effluent flow rate must match F_0 . Consequently, the
 339 residence times of MM and M in the reactor vessel depend on F_0 and F_4 that together determine
 340 ϕ_{II} . By the same token, it is obvious that RS1 offers no improvement over the stand-alone CSTR
 341 in terms of selectivity (Eq. (34) in Table 1) because the residence time of products in RS1 equals
 342 that of an ideal CSTR. Increasing ϕ_{II} improves the selectivity in RS2. The longer the space-time,
 343 the higher is the benefit of using RS2 over CSTR or RS1.

344



345 Figure 3. Purity of MM of product stream (left) and total mass concentration, w , in the reactor
 346 relative to the feed (right) for the stand-alone CSTR (black), RS1 (blue), and RS2 (red).
 347 Parameter values as in Fig. 2.

348

349 Since both PR and PU are maximal at low $k\tau_0$ (see Figs. 2 and 3), it is concluded that the reactor–
 350 separator processes should be operated in this region. The fact that Separator I rejects MMM
 351 completely causes a potential problem, however. As observed on the right in Fig. 3, the total
 352 concentration is constant in the stand-alone CSTR, but it becomes very high in RS1 when F_0 is
 353 large relative to the reaction rate (*i.e.*, low $k\tau_0$). This is detrimental in practice as it may lead to
 354 very high viscosity or precipitation of solutes. Such issues can be mitigated by using a more
 355 dilute feed, but this obviously leads to lower productivity.

356 In contrast, using RS2 to recycle the solvent offers a means to reduce the total concentration
 357 without compromising productivity. The cause of this is the same as that of enhanced purity –
 358 solutes that pass Separator I are removed more efficiently from the reactor. As observed in Fig.
 359 3, the solution in the reactor is significantly more dilute in a RS2 with large ϕ_{II} than in a CSTR.

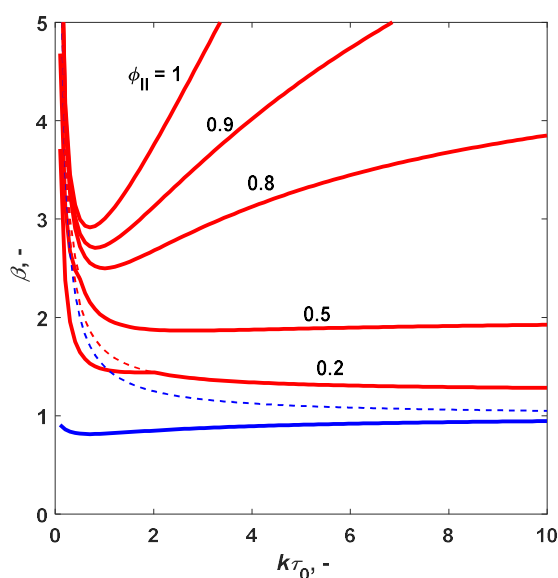
360

361 Against this background, a proper comparison of the productivities of the process schemes is
 362 obtained when the total mass concentration in RS1 and RS2 equals that in the stand-alone CSTR.
 363 In this case, the feed to RS1 must in fact be diluted to such a large extent that the productivity
 364 falls below that of the stand-alone CSTR. This is observed in Fig. 4. The feed to RS2, on the
 365 other hand, must be diluted only for such combinations of ϕ_{II} and $k\tau_0$ that lead to increasing
 366 concentration in the reactor, *i.e.* when $w_{R,tot}/w_0$ is above the black horizontal line in the figure.
 367 For $\phi_{II} = 0.20$, this means values below $k\tau_0 \approx 2$. With high internal solvent recycling, however,
 368 only the range of high fresh feed flow rates requires diluting the feed (*e.g.*, the range $k\tau_0 < 0.13$

369 for $\phi_{II} = 0.80$). The dashed curves in Fig. 4 represent β values in a situation where the total
 370 concentration is not a limiting factor (see Fig 2).

371 Note that, even though RS1 gives lower PR than a stand-alone CSTR for a given $k\tau_0$, process
 372 RS1 achieves higher purities PU (see Fig. 3) for the same total concentration.

373



374

375 Figure 4. Productivities in RS1 (blue) and RS2 (red) relative to the stand-alone CSTR for equal
 376 total mass concentrations in the reactor vessels. Dashed lines show the case where total
 377 concentration is unconstrained for reference (see Fig. 2). Parameters values as in Fig. 2.

378

379 The analysis presented above shows that reactor–separators do not automatically outperform a
 380 conventional conversion by a stand-alone CSTR. The aspect of increasing concentration in the
 381 reactor, which can be a serious issue, can be eliminated by recycling the solvent as is done in
 382 RS2. An alternative to this could be to use a bleed stream that matches the feed flow rate, as
 383 shown by [26]. The authors studied the depolymerization of inulin by an immobilized exo-type
 384 inulinase enzyme to produce the monosaccharide fructose in a reactor–separator–recycle process.
 385 Recovering the monosaccharide from the reactor occurred via diffusion through a size-selective
 386 membrane. Unreacted inulin and higher oligosaccharides were recycled to the reactor. Flooding
 387 of the reactor was prevented by using a discharge flow with no separator. This leads, however, to
 388 low yields, especially at large recycle ratios. Another strategy is to feed pure solvent to the
 389 reactor as chosen by Gan et al. [22] in enzymatic hydrolysis of cellulose. This is equivalent to
 390 diluting the feed to RS1, and obviously leads to diluted product stream.

391

392 The analysis based on ideal reactors and separators presented above reveals that reactor-
 393 separator-recycle processes like scheme RS2 may significantly improve all relevant performance
 394 indicators. There are some practical issues that may arise, however. Secondary effects such as

395 the influence of increasing viscosity on k can make RS1 even worse relative to stand-alone
 396 CSTR than predicted under ideal conditions. In addition, the total concentration in stream 2
 397 (reactant recycle) may become large when F_3 is large. This can be mitigated by increasing F_1 and
 398 operating Separator I with lower ϕ_I , but this increases energy consumption. Until now, the
 399 separation units were regarded ideal (*i.e.*, sharp). Even if they could be operated with a constant
 400 ϕ , in practice χ is affected by several factors depending on the unit operation and solution
 401 composition. In the case of membrane-based reactor–separators and biobased feeds, the most
 402 notable effects are concentration polarization [33] and fouling [34]. Therefore, in the next
 403 section, the role of separation efficiency is studied in detail.

404

405 **4. Degradation of polymers to a product fraction with controlled DP range**

406 If the raw material is a large polymer (or a mixture of large polymers) rather than an oligomer, it
 407 is hardly profitable to aim at producing a single degradation product molecule. In order to
 408 achieve a reasonable yield, the target is typically a mixture of polymers within a controlled size
 409 range.

410 The above analysis of the oligomer degradation system shows that the RS2 scheme has the best
 411 performance of the configurations studied. Therefore, production of polymer degradation
 412 products with a controlled size distribution is studied here using RS2 only.

413 In a sharp Separator I, the molecules smaller than or equal to a size DP^* pass through but larger
 414 molecules are completely rejected.

$$415 \quad \chi_1(DP) = \begin{cases} 1, & DP \leq DP^* \\ 0, & DP > DP^* \end{cases} \quad (35)$$

416

417 When Separator I is non-sharp, the concentration ratio χ_1 is not strictly 0 or 1. For the sake of
 418 illustration we assume that $\chi_1(DP)$ is a monotonic, symmetric and centered function at a given
 419 degree of polymerization $DP_{0.5}$. A convenient function for this purpose is the hyperbolic tangent.
 420 The sharpness of the separator can be adjusted by specifying the value of χ_1 at one additional
 421 arbitrary degree of polymerization. In other words, by specifying $\chi_1 = 0.5$ at $DP = DP_{0.5}$ and
 422 $\chi_1 = \gamma$ at $DP = DP_\gamma$, the separation performance of Separator I is calculated from

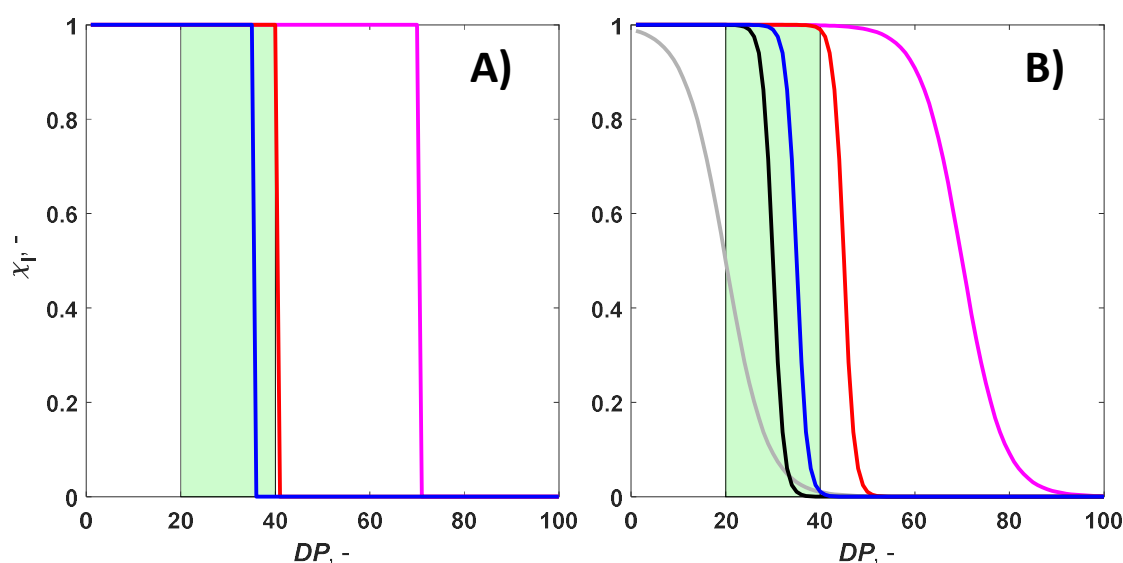
$$423 \quad \chi_1(DP) = \frac{1}{2} - \frac{1}{2} \tanh\left((DP - DP_{0.5}) \frac{\tanh^{-1}(2\gamma - 1)}{DP_\gamma - DP_{0.5}} \right), \quad \gamma > 0.5 \quad (36)$$

424

425 Several cases where Separator I is sharp are analyzed in the next section, followed by more
 426 realistic systems where χ_1 decreases gradually with increasing molecular size. The concentrations
 427 in the reactor and in the effluent stream were calculated by using the equations derived in Section
 428 2.2. A monodisperse polymer with $DP = 100$ was used as feed and the degradation products in

429 the range $20 \leq DP \leq 40$ were considered as the product fraction. Along the results of the
 430 previous section, the space-time of the reactor and the solvent recycle ratio were varied within
 431 limits $0 \leq k\tau_0 \leq 0.5$ and $0 \leq \varphi_{II} \leq 1$. It was also required that the total mass concentration in the
 432 reactor must not exceed the feed concentration, *i.e.* $w_{\text{tot}}^R \leq w_{\text{tot}}^{\text{feed}}$. Owing to first order kinetics of
 433 the degradation reactions, the feed concentration has no effect on the results discussed here.
 434 Figure 5 illustrates the separation characteristics of sharp and non-sharp Separator I for the
 435 cases that are analyzed below.

436



437

438 Figure 5. Rejection characteristics of sharp (A) and non-sharp (B) Separator I in RS2 according
 439 to Eq. (35). The green shaded area marks the target DP range. Parameters of Eq. (35) for sharp
 440 separator: blue: $DP^* = 35$, red: $DP^* = 40$, magenta: $DP^* = 70$. Parameters of Eq. (36) for the non-
 441 sharp separator: $\gamma = 0.99$; magenta: $DP_{0.5} = 70$, $DP_{0.99} = 90$; red: $DP_{0.5} = 45$, $DP_{0.99} = 50$, blue:
 442 $DP_{0.5} = 35$, $DP_{0.99} = 40$; black: $DP_{0.5} = 30$, $DP_{0.99} = 35$; gray: $DP_{0.5} = 20$, $DP_{0.99} = 40$.

443

444 4.1. Sharp Separator I

445 The influence of the operating parameters on PR and PU are displayed in Fig 6. The gray shaded
 446 areas are not feasible operating points because the total mass concentration in the reactor would
 447 exceed the feed concentration.

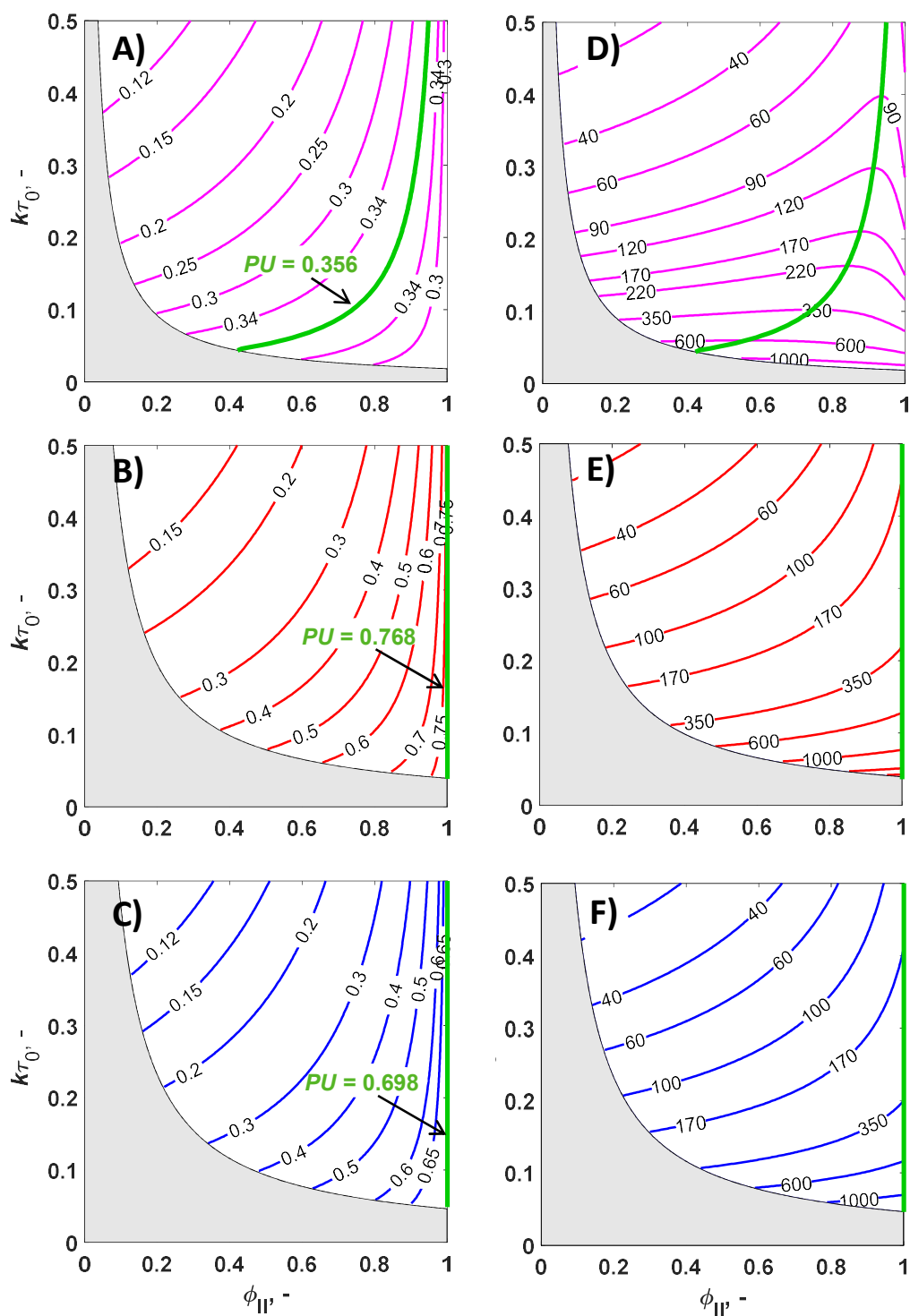
448 The green isolines in Fig. 6 show the combinations of operating parameters that yield the highest
 449 achievable PU in each case. Within the region to the left of the maximum purity isoline, moving
 450 the operating point towards low $k\tau_0$ results in increasing purity. On the right-hand side of it, the
 451 opposite is true. For systems where Separator I does not pass any molecules larger than the target
 452 fraction (red and blue curves in Figs. 6B, C, E, F), maximum PU and PR are achieved by
 453 operating the RS2 with as high recycle ratio as possible. This is because the product molecules
 454 should be removed from the system as soon as they are formed to avoid further degradation.

455 When some unreacted molecules larger than the target fraction can pass Separator I (Fig. 6A and
456 B, $DP^* = 70$), the optimum recycle ratio depends on $k\tau_0$. Too high ϕ_{II} reduces purity and
457 productivity by carrying unreacted reactants into the effluent. It is noteworthy that above a
458 certain $k\tau_0$ value, the optimum ϕ_{II} maximizes both PU and PR simultaneously (see Fig. 6D). The
459 limiting $k\tau_0$ value is the point where the green isoline meets the gray unfeasible region. Below
460 this, the productivity can be increased by increasing the solvent recycling rate only at the cost of
461 decreasing purity.

462 It is tempting to conclude from these data that sharp Separator I should always be chosen (if it
463 exists) such that DP^* equals the largest molecules in the product fraction. This option (Figs. 6B
464 and 6E) does indeed yield highest purity and productivity – but only if an arbitrarily large solvent
465 recycle ratio can be used. If solvent recycle ratio is restricted to relatively low values (*e.g.*, $\phi_{II} <$
466 0.2) due to the capacity or the operating costs of Separator II, letting some of the unreacted large
467 molecules pass Separator I is beneficial for both PR and PU . The lowest performance is observed
468 when part of the product molecules is retained by Separator I.

469

470



471
 472 Figure 6. Effluent purity (A, B, C) and productivity (D, E, F) for process RS2 in the case of a
 473 sharp Separator I. The green isolines show the operating points for highest achievable purity.
 474 Separator I cut-off (DP^* in Eq. (35)): magenta = 70, red = 40, blue = 35.

475

476 4.2 Non-sharp Separator I

477 In practical systems, and in particular when using membrane processes, Separator I is likely to be
 478 non-sharp. The shape and the position of $\chi_1(DP)$ can be expected to affect process performance.

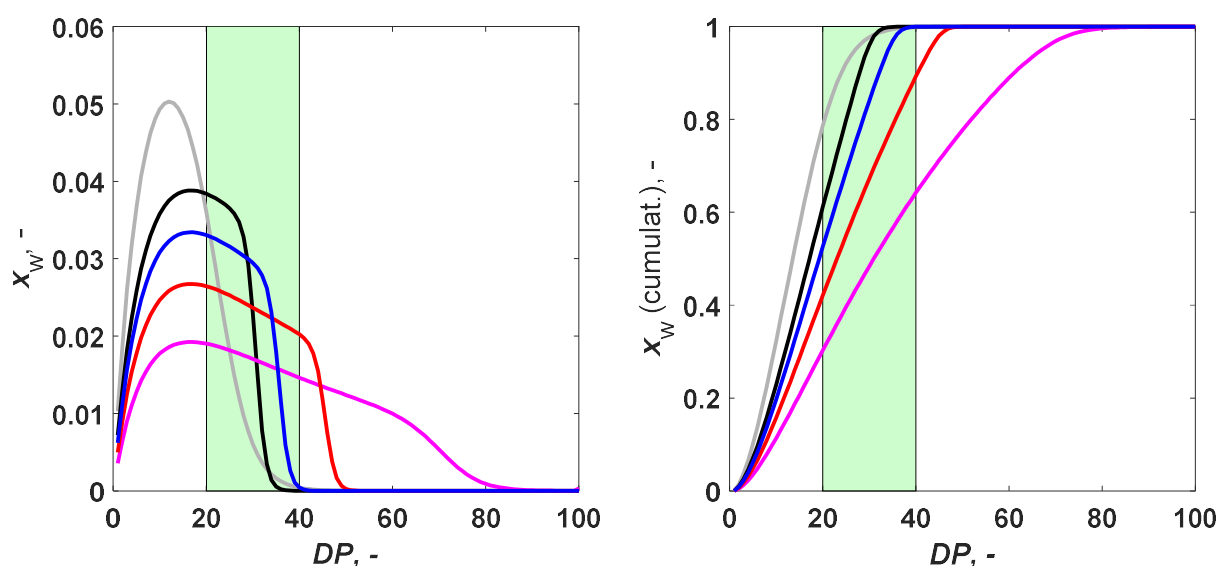
479 In order to analyze this, two relatively broad distributions in χ_1 as well as three narrow
 480 distributions in χ_1 were used. The difference $DP_{0.99} - DP_{0.5} = 5$ was regarded as narrow and
 481 $DP_{0.99} - DP_{0.5} = 20$ as broad in this context.

482 As illustrated in Fig. 5, the broad distributions were selected such that only molecules within or
 483 below the target DP range can pass the separator (gray curves, $DP_{0.5} = 20$) or such that only the
 484 very large molecules are completely rejected (magenta curves, $DP_{0.5} = 70$).

485 One of the narrow distributions (black, $DP_{0.5} = 30$) is centered on the mean of the target DP
 486 range but some product molecules can pass the separator. Another narrow distribution (blue,
 487 $DP_{0.5} = 35$) is set such that no molecules larger than $DP = 40$ pass the separator but, because the
 488 separator is non-sharp, the largest target molecules are partially rejected. The third narrow
 489 distribution (red, $DP_{0.5} = 45$) is set such that all target molecules but also a small amount of
 490 unreacted large molecules pass the separator.

491 Fig. 7 displays the effect of separator characteristics on the composition of the effluent at a single
 492 operating point ($\phi_{II} = 0.80$, $k\tau_0 = 0.15$). As expected, the higher the $DP_{0.5}$ value, and the broader
 493 the distribution of χ_1 , the broader is the molecular size distribution in the effluent. On the other
 494 hand, $DP_{0.5} = 20$ is clearly suboptimal as too much of the product molecules degrade to smaller
 495 impurities. To get a more complete picture of the performance of the RS2 process, a relevant part
 496 of the operating parameter plane (ϕ_{II} , $k\tau_0$) is analyzed below.

497



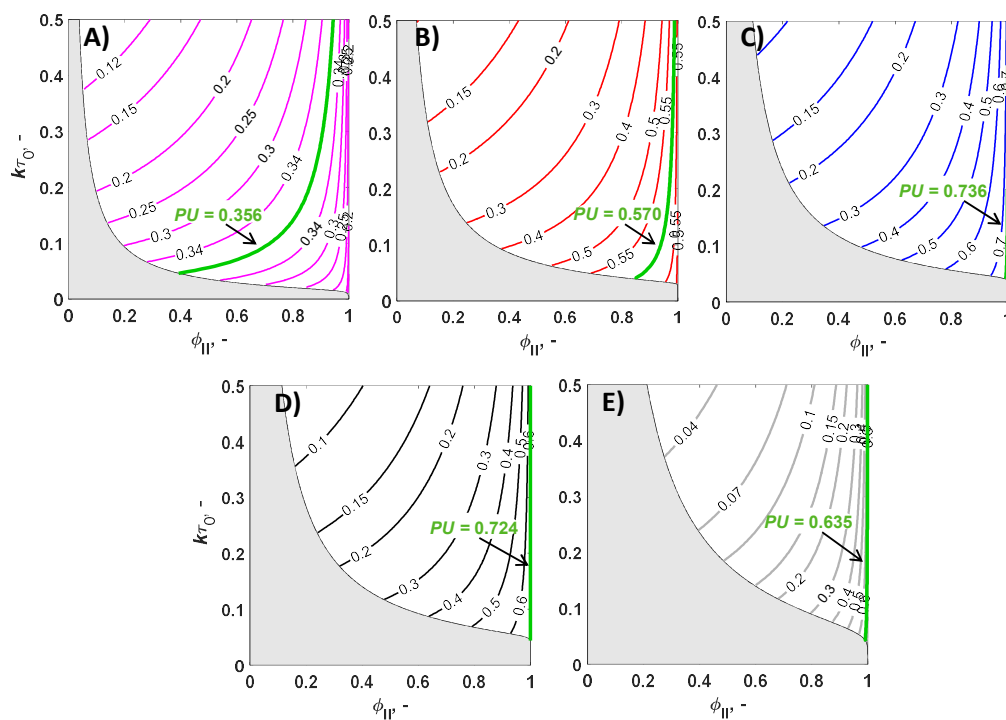
498 Figure 7. Weight-based differential (left) and cumulative (right) molecular size distributions in
 499 the effluent of RS2 in the case of non-sharp Separator I. Operating parameters: $k\tau_0 = 0.15$; $\phi_{II} =$
 500 0.80 . Parameters of Eq. (36) are given in caption to Fig. 5.

501
 502 The influence of the operating parameters on PR and PU is displayed in Figs. 8 and 9. Again, the
 503 gray shaded areas are not feasible because the total concentration in the reactor would exceed the
 504 feed concentration. For a given fresh feed composition and kinetics, and when Separator II
 505 recycles pure solvent, maximum PU is determined by the rejection characteristics of Separator I
 506 only. For each $k\tau_0$, there is a single ϕ_{II} where purity is maximized.

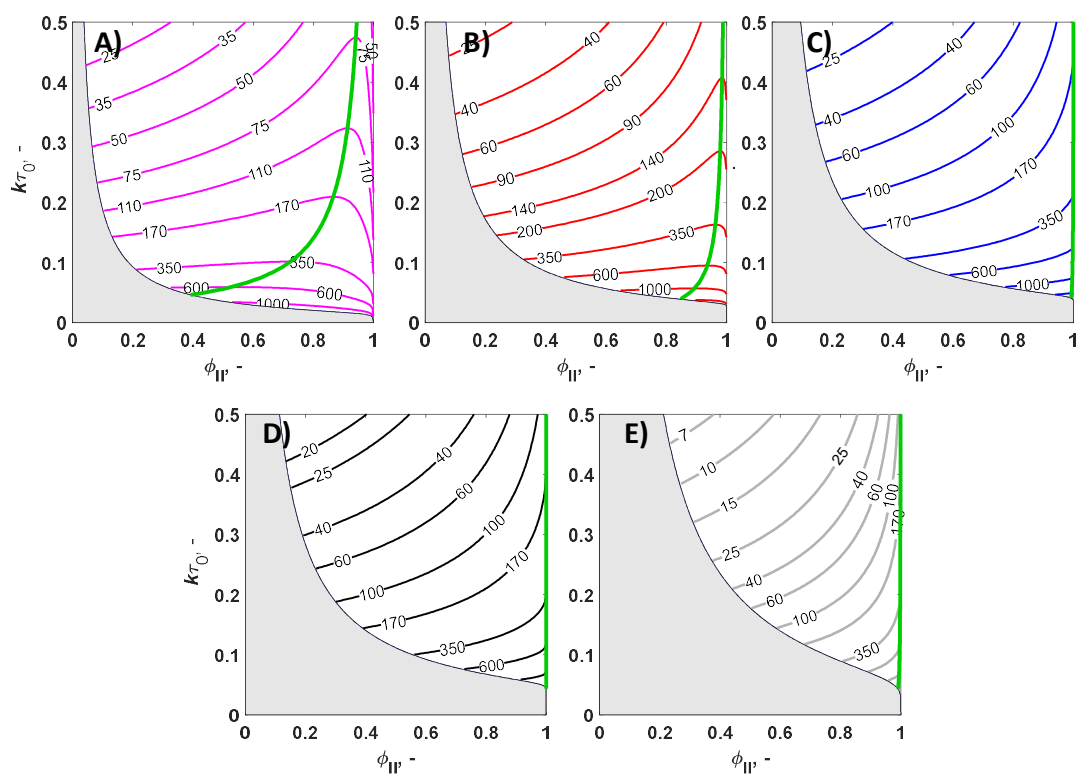
507 Like with sharp Separator I, maximum PU is achieved by operating at as high recycle ratio as
 508 possible when the separator does not pass molecules larger than the target fraction (subfigures C,
 509 D and E). When unreacted large molecules can pass Separator I (subfigures A and B), the
 510 optimum solvent recycle ratio depends on $k\tau_0$. Bringing the separator's cut-off closer to the upper
 511 limit of the target DP range increases PU and PR .

512

513

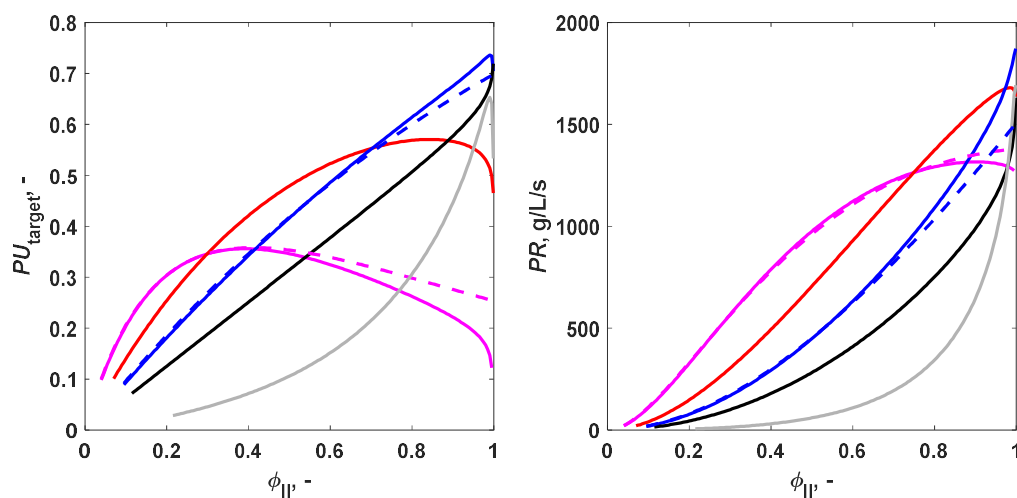


514
 515 Figure 8. Effluent purity in RS2 in the case of a non-sharp Separator I. The green isolines
 516 correspond to maximum purity. Parameters of Eq. (36) are given in the caption to Fig. 5.



517
 518 Figure 9. Productivity of RS2 in the case of a non-sharp Separator I. The green isolines
 519 correspond to maximum purity. Parameters of Eq. (36) are given in the caption to Fig. 5.

520
 521 While the performance of RS2 can be improved by recycling more solvent, increasing the
 522 capacity of Separator II is likely more expensive than changing $k\tau_0$. It is therefore best to choose
 523 the operating point on the boundary of the unfeasible operating parameter region. The behavior
 524 of PU and PR along this boundary are shown in Fig. 10. It is noteworthy that an RS2 can reach
 525 almost the same productivity irrespective of the characteristics of Separator I. There are large
 526 differences in the required ϕ_{II} , however. Very high ϕ_{II} is needed especially when Separator I does
 527 not pass all small molecules through. It is concluded that, when operating Separator II at high ϕ_{II}
 528 is expensive, choosing a Separator I that passes larger molecules through is preferred for high
 529 purity and productivity.



530

531 Figure 10. Effect of solvent recycling on purity of the effluent stream and productivity when RS2
 532 is operated at the limit $w_{\text{tot}}^{\text{R}} = w_{\text{tot}}^{\text{feed}}$. Dashed line: sharp Separator I; solid lines: non-sharp
 533 Separator I. χ_1 parameters are given in Fig. 5.

534

535 Figures 6 to 10 allow comparison of sharp and non-sharp separators in two cases. The magenta
 536 curves correspond to situation where only large molecules are rejected ($DP^* = 70$, $DP_{0.5} = 70$). It
 537 is observed that the highest achievable PU with sharp and non-sharp separators are practically
 538 identical ($PU = 0.356$ vs. 0.356). The sharp separator offers higher purity only at high ϕ_{II} values.
 539 Productivity is practically not affected by the width of the χ_1 distribution.

540 The blue curves correspond to Separator I retaining part of the product molecules ($DP^* = 35$, $DP_{0.5}$
 541 $= 35$). In this case, the sharp separator gives somewhat lower purity and productivity than the non-
 542 sharp separator ($PU = 0.698$ vs. 0.736). Even though $DP^* = DP_{0.5}$ here, and χ_1 distribution from
 543 Eq. (11) is symmetric, the non-sharp separator passes a larger *mass fraction* of product molecules
 544 through because retention is defined using molar concentration ratios. The practical meaning of
 545 these results is that the performance of RS2 is not very sensitive to the selectivity of the separator
 546 (width of the χ_1 distribution).

547

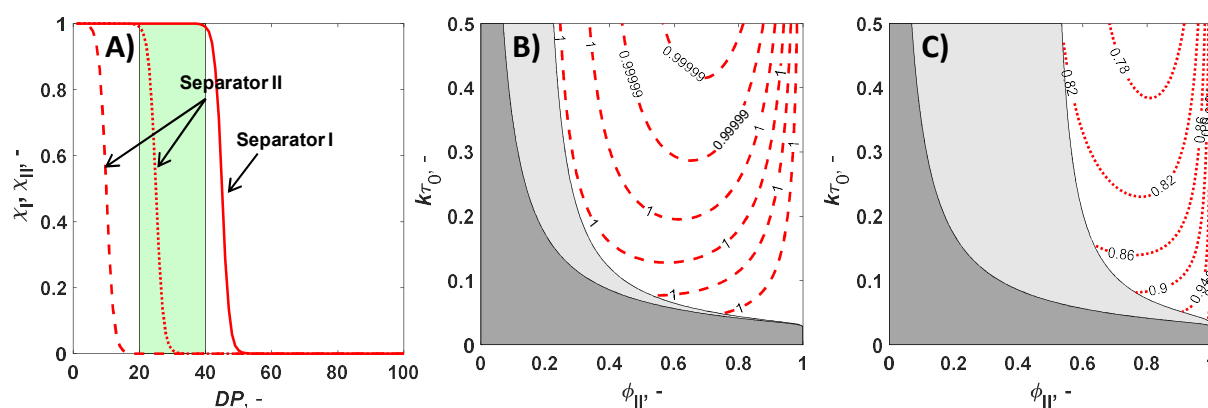
548 4.3 Incomplete rejection at Separator II

549 In some practical cases, Separator II may be operated such that the recycled solvent is not pure
 550 but contains some solutes. Typically, the solutes passing this separator are the smaller molecules.
 551 Two scenarios, illustrated in Fig. 11A, are studied to understand how this affects the range of
 552 feasible operating parameters and the product purity.

553 The solid line in Fig. 11A shows the rejection characteristics at Separator I used in both
 554 scenarios. In the first scenario (dashed lines), part of the molecules smaller than the product
 555 fraction can pass Separator II, and are recycled back to the reactor with the solvent. In the second
 556 scenario (dotted lines), also part of the target molecules are recycled with the solvent.

557 As expected, incomplete rejection of solutes at Separator II leads to accumulation of mass in the
 558 reactor. Consequently, higher solvent recycle ratios are needed to prevent the increase of w_R^{tot}
 559 beyond the limiting value. This is observed in Figs. 11B and 11C as shrinking of the feasible
 560 operating parameter regions. The increase in the required solvent recycling rate can be quite
 561 substantial. At $k\tau_0 = 0.1$, for example, the minimum solvent recycle is 50% of the fresh feed flow
 562 rate when pure solvent is recycled and 250% when part of the target molecules pass to the
 563 recycle stream (Fig. 11C, $DP_{0.5} = 25$).

564



565

566 Figure 11. Effect of incomplete rejection at Separator II on effluent purity. A) Properties of the
 567 separators. Solid line: χ_I ($DP_{0.5} = 45$, $DP_{0.99} = 50$). Dashed line: χ_{II} ($DP_{0.5} = 10$, $DP_{0.99} = 15$); dotted
 568 line: χ_{II} ($DP_{0.5} = 25$, $DP_{0.99} = 30$). B) and C) PU relative to PU with recycling of pure solvent. Dark
 569 gray area is unfeasible when pure solvent is recycled. Light gray area is unfeasible in the case of
 570 incomplete rejection at Separator II.

571

572 It is interesting that the purity of the effluent is not affected by incomplete rejection when all
 573 molecules that can pass Separator II are smaller than the target fraction (Fig. 11B). According to
 574 the present reaction scheme (random degradation of homologues, irreversible 1st order reactions),
 575 accumulation of small impurity molecules in the reactor–separator unit does not affect the
 576 reactions of the larger molecules. Consequently, the total mass concentration of impurities with
 577 $DP < 20$ is the same as when recycling pure solvent only. It is worth noting, however, that the
 578 molecular weight distribution of the impurities is different when they can accumulate in the
 579 reactor.

580 When Separator II lets part of the product molecules accumulate in the system, effluent PU may
 581 be reduced up to 20% relative to pure solvent recycling (Fig. 11C). The cause is, of course,
 582 increased residence time of the target molecules. This can be mitigated by using very high
 583 recycle ratios ($\phi_{II} > 0.95$) or short space-time ($k\tau_0 < 0.05$) because this reduces the formation of
 584 small molecules. The nonlinear behavior of PU relative to the case of pure solvent recycling
 585 stems from varying molecular weight distribution in the reactor.

586 The practical meaning of these results is that the operating strategy and/or the separation material
 587 properties of Separator II is not as restrictive as it may appear. The RS2 concept can tolerate

588 accumulation of small impurity molecules, provided that sufficiently large ϕ_{II} can be used. In
589 some process options for Separator II, such as using membrane filtration, relaxing the
590 requirement for very high retention of small molecules typically improves the permeate flux and
591 enables achieving higher ϕ_{II} with reduced energy consumption. In case of size-exclusion
592 chromatographic separation, the front of the profile would contain large molecules that are
593 recycled whereas the tail would contain small impurity molecules. The above results suggest that
594 allowing overlap of profiles from consecutive cycles increases productivity by alternatively
595 reducing the size of the separation column relative to the reactor or by shortening the cycle time
596 (*i.e.*, time interval between consecutive feed pulses).

597 If accumulation of small molecules through Separator II causes a problem that cannot be
598 resolved by increasing solvent recycling, an additional bleed stream could be introduced in the
599 solvent recycle loop. If Separator II rejects the product molecules, this would increase *PU*
600 without decreasing yield and the small molecules could be recovered in high purity as a
601 byproduct. Of course, the cost of additional make-up solvent must be considered.

602

603 5. Conclusion

604 Operation of recycle-integrated reactor-separator processes for production of oligomers and
605 polymers with controlled size distribution by degradation of larger molecules was analyzed
606 theoretically. Two continuous reactor separator schemes were compared with a conventional
607 stand-alone CSTR. Closed-form solutions for composition in the reactor vessels and the process
608 effluent were derived for a system of serial-parallel first-order reactions.

609 It was shown for a simple three-molecule system that a reactor-separator without solvent
610 recycling (RS1) may be less productive than a conventional CSTR if there is an upper limit for
611 the total concentration in the reactor vessel. Since this process is equivalent to a multifunctional
612 reactor, it can be sub-optimal for such reaction problems to apply, for example, a dead-end
613 membrane reactor to retain large reactants. Introducing an additional separator to recover product
614 molecules and to recycle the solvent (RS2) significantly improves both product purity and
615 productivity. Solvent recycling introduces an additional degree of freedom and decouples the
616 feed rate and the residence time of the product molecules.

617 A more general case, degradation of a polymer to a mixture of smaller molecules with desired
618 molecular size distribution, was also studied. The effect of the characteristics of the separators on
619 process performance was analyzed. The results obtained show that recycle-integrated reactor-
620 separator processes for polymer degradation are beneficial even when the separators are non-
621 sharp. It was shown that increasing the solvent recycle rate improves productivity and product
622 purity when product molecules are only partially rejected by Separator I. In addition, it was
623 found that the recycled solvent does not need to be pure but can contain molecules smaller than
624 the target fraction. Incomplete rejection at Separator II is not an issue, if the product molecules
625 are not recycled to a large extent.

626 These results are relevant for the development of optimal reactor-separator processes to produce
627 biobased molecules with controlled molar mass distribution by degradation of large biopolymers.

628 In addition, as demonstrated with the ternary system, they are relevant also for reactions of
629 oligomers.

630

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635

Latin letters

| | |
|-------------|--|
| c | mole concentration, mol m^{-3} |
| \bar{c} | array of molar concentrations, mol m^{-3} |
| DP | degree of polymerization, – |
| DP^* | cut-off DP of a sharp separator, – |
| DP_γ | degree of polymerization characterizing a non-sharp separator, – |
| F | volumetric flow rate, $\text{m}^3 \text{s}^{-1}$ |
| j | index, – |
| k | reaction rate constant, s^{-1} |
| n | degree of polymerization, – |
| N | highest degree of polymerization in the mixture, – |
| M_w | molar mass, kg mol^{-1} |
| PR | productivity, $\text{kg m}^{-3} \text{s}^{-1}$ |
| PU | purity, – |
| p_1 | index of the largest product molecule, – |
| p_2 | index of the smallest product molecule, – |
| r | reaction rate, $\text{mol m}^{-3} \text{s}^{-1}$ |
| S | selectivity, – |
| V | volume, m^3 |
| w | mass concentration, kg m^{-3} |
| Y | yield, – |

Greek letters

| | |
|----------|--|
| β | productivity ratio for two process options, – |
| γ | mass splitting parameter characterizing a non-sharp separator, – |
| ϕ | flow splitting parameter, – |
| χ | mass splitting parameter, – |
| τ | space time of the reactor, s |

Subscripts

| | |
|-----|---|
| 0 | feed |
| out | outlet of the reactor–separator process |
| R | reactor vessel |
| tot | total, including all species |

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