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RESEARCH ARTICLE

MWD design in a series of CSTRs with living polymerisation reactions

Eszter Farkas / *Zsolt György* Meszéna

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Abstract

In previous papers of this work methodologies have been established i) to predict the molecular weight distribution (MWD) of living polymerisation processes in various reactor configurations, ii) and – in a reversed calculation process – to design reactor parameters and feed profiles for a single CSTR or a tubular reactor to meet a target MWD.

In this paper a model of a series of continuous stirred tank reactors (CSTRs) with various initiator and monomer feed strategies have been used to establish i) the possible MWD shapes with constant feed, ii) the MWD with the lowest possible polydispersity index, and iii) a methodology to design multimodal MWDs with a continuous steady state process.

Both the MWD prediction and the design methodologies use a simplified, very fast, direct algorithm, well suited for control purposes.

Keywords

polymer · MWD · calculation · living · CSTR · cascade

Eszter Farkas

Department of Inorganic and Analytical Chemistry, BME, 1521 Budapest Pf 91, Hungary

e-mail: farkas.eszter.hu@gmail.com

Zsolt György Meszéna

Department of Inorganic and Analytical Chemistry, BME, 1521 Budapest Pf 91, Hungary

1 Introduction

It is evident that polymer properties are related to the full molecular weight distribution (MWD). However, in most industrial processes, the average chain length or molecular weight is used to characterize the product. It has been shown that even the second moment of the MWD carries information not available from the reactor temperature profile or monomer conversion, and this information can be vital to control parameter tuning or product characterization [6].

In practice, the full MWD envelope of a polymer is rarely established, since precise calculations require an excessive computational power. Approximation methods provide a trade-off between calculation efficiency and accuracy, and have always been central to this field of research. It has been previously established that

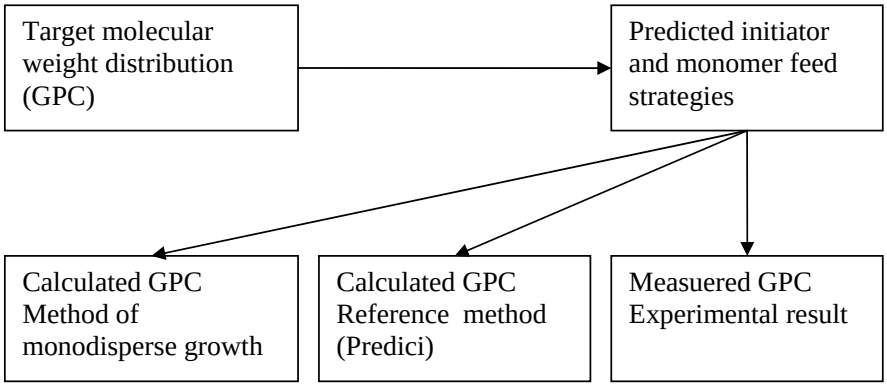
1 The MWD from a living polymerisation process carried out in various reactor configurations with constant or unsteady feed profiles can be very well approximated with a simplified, very fast, direct algorithm, the method of monodisperse growth (Gosden et al, 1995). The effect of unsteady feeds as well as the reactor residence time distribution is taken into account precisely. The burden of the precise MWD calculations is eased off by simplifying the multi-step chain growth to a single-step (monodisperse) process.

2 The calculation methodology can be readily reversed. Based on the reversed calculation sequence, a design algorithm has been established in order to predict reactor parameters and feed profiles to meet a target MWD [2, 9]. The concept of the design process is shown in Fig. 1.

3 The shape of possible MWDs with a single CSTR is restricted to the Schulz-Flory distribution. On the long run, if the product is collected, any unsteady feed profiles – if applied periodically – produce a Schulz-Flory distribution [2]. Consequently, there is not much scope left for MWD design with a single CSTR.

4 No such theoretical restrictions apply to a process utilizing a tubular reactor, a wide range of MWD shapes are feasible [2, 7]

Fig. 1. MWD design methodology



In practice, however, a series of CSTRs are preferred to a tubular reactor for the ease of handling, control and for higher throughput rates (Farkas and Meszéna, 2008) [3]. In this paper an MWD design methodology has been established using a series of CSTRs with various monomer and initiator feed strategies. It is shown that

1 The method established converges to the theoretically possible lowest dispersity MWD, if the number of stages is increased.

2 The minimal dispersity for a given reactor configuration can be predicted.

3 Multimodal MWDs are possible to design if several initiator input points and, consequently, different residence times of growing chains are used. The derivation of initiator input positions and input profiles is presented.

4 The number of stages can be used as a design parameter, if desired.

2 Method

2.1 MWD prediction for a steady state CSTR cascade

In the example shown four stages have been used. The method is generic and not restricted to a particular number of stages used. Notations used are shown in Fig. 2.

The steady state product of the first reactor has a Schulz Flory MWD:

$$\bar{P}_1(j) = \frac{I_{in}}{Da_1} \cdot \left(\frac{Da_1}{Da_1+1}\right)^j \tag{1}$$

where I_{in} is the inlet initiator concentration and Da_1 is the first stage Damkohler number:

$$Da_1 = k_{p,1}\, M_{1,in}\, \tau$$

The output of the first stage is fed to the second one. The product MWD from the second stage can be approximated with method of mondisperse growth [9] :

$$\bar{P}_2(j) = \underbrace{\int_{t'=t_0}^{t_{end}} \bar{P}_1\left(j-\mu\left(t_{end}-t'\right)\right)}_{q(t')} \underbrace{\frac{1}{\tau_2} e^{-\frac{t_{end}-t'}{\tau_2}}}_{E(t-t')} dt'$$

Central to the method is the simplification that in the time frame t' to t_{end} every chain is extended with the same $\mu(t_{end}-t')$ length, out of which the fraction given by the internal age distribution

$$E(t-t') = \frac{1}{\tau_2} e^{-\frac{t_{end}-t'}{\tau_2}}$$

stays in the reactor till t_{end}. Consequently, the amount of chains of length j is an integral of these fractions over the time period t_0 to t_{end} in question.

After substituting the initial MWD for $\bar{P}_1$ and changing the parameter of integration from time to chain length

$$\mu = Da(t'-t_0) \tag{2}$$

integration can be carried out analytically (Da is constant in the steady state) and the MWD from the second stage is

$$\bar{P}_2(j) = \int_{\mu=0}^{j} \frac{I_{in}}{Da_1} \cdot \left(\frac{Da_1}{Da_1+1}\right)^{j-\mu} \frac{1}{Da_2} e^{-\frac{\mu}{Da_2}} d\mu$$

It is noted that chain length is treated in this work as a continuous variable [9].

Since $Da >> 1$ in practical processes the approximation $\ln(x) \approx -1+x$ can be applied to result

$$\bar{P}_2(j) = \frac{I_{in}}{Da_1 \cdot Da_2} \left(\frac{Da_1}{Da_1+1}\right)^j$$

$$\int_{\mu=0}^{j} e^{\frac{\mu}{1+Da_1}} \cdot e^{-\frac{\mu}{Da_2}} d\mu = \frac{\bar{P}_1(j)}{Da_2} \int_{\mu=0}^{j} e^{\frac{\mu}{Da_1+1}} \cdot e^{-\frac{\mu}{Da_2}} d\mu$$

After integration the number chain length distribution (NCLD) from the second stage is MWD design in a series of CSTRs

$$\bar{P}_2(j) = \frac{(1+Da_1)\,\bar{P}_1(j)}{Da_1+1-Da_2} \cdot \left(1-e^{-j\cdot\frac{Da_1+1-Da_2}{(1+Da_1)Da_2}}\right)$$

if $Da_1+1 \neq Da_2$

$\bar{P}_2(j) = \frac{j\bar{P}_1(j)}{Da_2}$, if $Da_1+1 = Da_2$

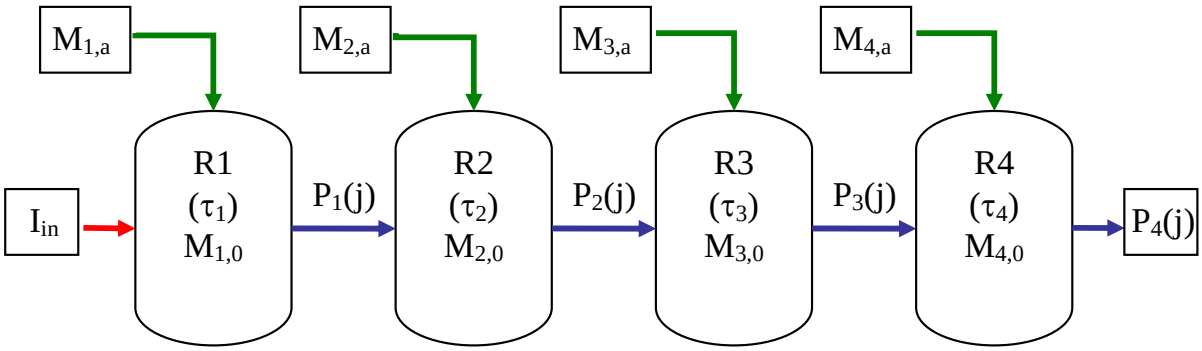


Fig. 2. CSTR cascade model with four stages

Similarly, the MWD from the third stage is

$$\bar{P}_3(j) = \int_{\mu=0}^{j} \bar{P}_2(j-\mu)\,\frac{1}{Da_3}e^{-\frac{\mu}{Da_3}}d\mu = \int_{\mu=0}^{j} \frac{(1+Da_1)}{Da_1+1-Da_2}\,\frac{I_{in}}{Da_1}\left(\frac{Da_1}{Da_1+1}\right)^{j-\mu} \left(1-e^{-(j-\mu)\cdot\frac{Da_1+1-Da_2}{(1+Da_1)Da_2}}\right)\frac{1}{Da_3}e^{-\frac{\mu}{Da_3}}d\mu.$$

With approximation $\ln(x) \approx -1 + x$:

$$\bar{P}_3(j) = \int_{\mu=0}^{j} \frac{(1+Da_1)}{Da_1+1-Da_2}\,\frac{I_{in}}{Da_1 Da_3}e^{\frac{-(j-\mu)}{Da_1+1}} \left(e^{-\frac{\mu}{Da_3}} - e^{-(j-\mu)\cdot\frac{Da_1+1-Da_2}{(1+Da_1)Da_2}-\frac{\mu}{Da_3}}\right)d\mu$$

and notations:

$$A = \frac{1}{Da_1+1} - \frac{1}{Da_3}, \quad B = \frac{1}{Da_2} - \frac{1}{Da_3},$$

$$C = \frac{1}{Da_2} - \frac{1}{Da_1+1}$$

the integral defining the MWD is simplified to

$$\bar{P}_3(j) = \int_{\mu=0}^{j} \frac{I_{in}}{Da_1 Da_2 Da_3}\cdot\frac{1}{C}e^{\frac{-j}{Da_1+1}}\left(e^{A\mu} - e^{-jC}e^{B\mu}\right)d\mu$$

After integration the MWD from the third stage is

$$\bar{P}_3(j) = \frac{1}{Da_2 Da_3}\cdot\frac{1}{C}\bar{P}_1(j)\cdot \left(\frac{1}{A}e^{Aj} - \frac{1}{B}e^{(B-C)j} - \frac{1}{A} + \frac{1}{B}e^{-jC}\right)$$

Similarly, the MWD from the fourth stage is

$$\bar{P}_4(j) = \int_{\mu=0}^{j} \bar{P}_3(j-\mu)\,\frac{1}{Da_4}e^{-\frac{\mu}{Da_4}}d\mu = \int_{\mu=0}^{j} \frac{I_{in}}{Da_1 Da_2 Da_3}\cdot\frac{1}{C}e^{\frac{-(j-\mu)}{Da_1+1}}\left(\frac{1}{A}e^{A(j-\mu)} - \frac{1}{B}e^{(B-C)(j-\mu)} - \frac{1}{A} + \frac{1}{B}e^{-(j-\mu)C}\right)\frac{1}{Da_4}e^{-\frac{\mu}{Da_4}}d\mu$$

With notation $D = \frac{1}{Da_1+1} - \frac{1}{Da_4}$ and after integration the MWD from the fourth stage is

$$\bar{P}_4(j) = \frac{1}{Da_2 Da_3 Da_4}\cdot\frac{1}{C}\bar{P}_1(j)\cdot \left(\left(\frac{B-A}{AB(D-A)} - \frac{1}{AD} + \frac{1}{B(C+D)}\right)e^{Dj} - \frac{1}{A(D-A)}e^{Aj} + \frac{1}{B(D-A)}e^{(B-C)j} + \frac{1}{AD} - \frac{1}{B(C+D)}e^{-jC}\right)$$

The monomer feed, $M_{1,in}$ necessary to the desired chain growth can be derived as

$$M_{1,in} = M_{1,0} + I_{in} + k_p \cdot M_{1,0} \cdot \tau_1 \cdot I_{in} = \frac{Da_1}{k_p\tau_1} + (1+Da_1)\cdot I_{in} \tag{3}$$

Due to the assumption of instantaneous initiation, no initiator is present in the product stream of the first reactor. Total polymer concentration is equal to the initiator input. The monomer feed concentration to the second stage, $M_{2,in}$ can be derived as

$$M_{2,in} = M_{2,0} - M_{1,0} + k_p \cdot M_{2,0} \cdot \tau_2 \cdot I_{in} = \frac{Da_2}{k_p\tau_2} + Da_2 \cdot I_{in} - \frac{Da_1}{k_p\tau_1} \tag{4}$$

Similarly, for any stage n (n > 1) the monomer feed concentration to stage n, $M_{n,in}$ is given by

$$M_{n,in} = M_{n,0} - M_{n-1,0} + k_p \cdot M_{n,0} \cdot \tau_n \cdot I_{in} = \frac{Da_n}{k_p\tau_n} + Da_n \cdot I_{in} - \frac{Da_{n-1}}{k_p\tau_{n-1}} \tag{5}$$

It is practical to assume that the necessary monomer concentrations just derived are maintained by sequential monomer addition to every stage. Consequently, the overall volumetric flow rate is increasing, the polymer concentration is decreasing stage by stage. The MWD formulas with volume correction are

$$\bar{P}_2(j) = \frac{W_1}{W_1+W_{2,M}}\,\frac{(1+Da_1)\,\bar{P}_1(j)}{Da_1+1-Da_2}\cdot \left(1-e^{-j\cdot\frac{Da_1+1-Da_2}{(1+Da_1)Da_2}}\right) \tag{6}$$

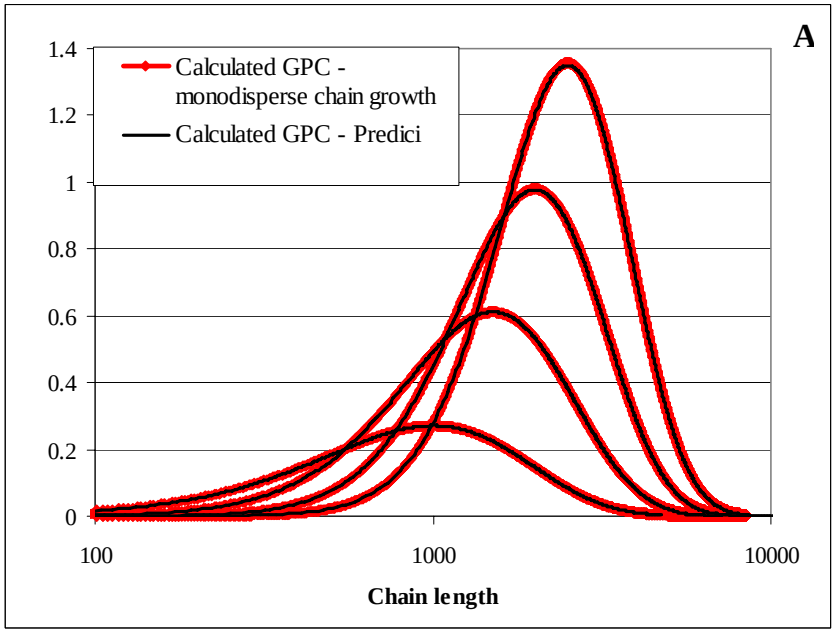


Fig. 3. MWD predictions for 4-stage CSTR cascade. Case A) Stage by stage Damköhler numbers are constant

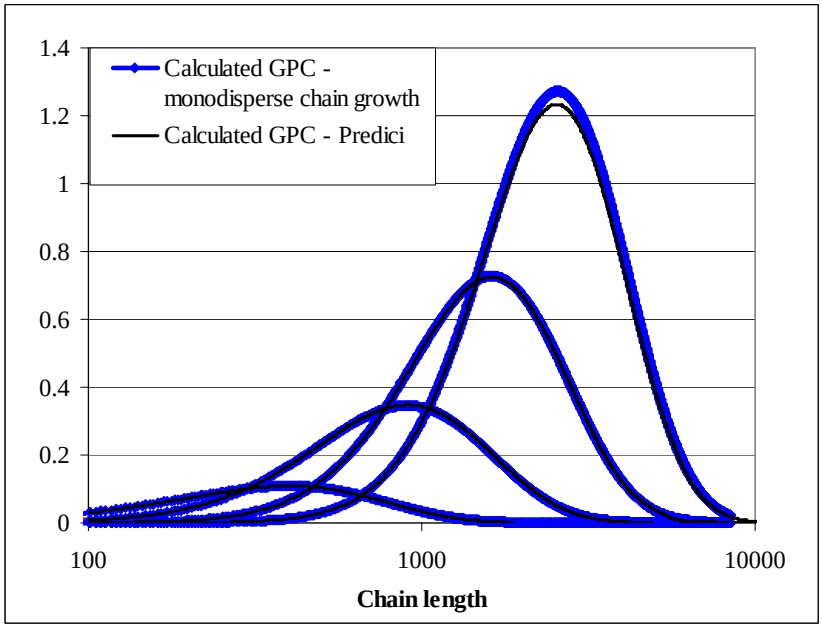


Fig. 4. MWD predictions for 4-stage CSTR cascade. Case B) Stage by stage Damköhler numbers are increasing

$$\bar{P}_3(j) = \frac{W_1}{W_1 + W_{2,M} + W_{3,M}} \frac{1}{Da_2 Da_3} \cdot \frac{1}{C} \bar{P}_1(j) \left(\frac{1}{A} e^{Aj} - \frac{1}{B} e^{(B-C)j} - \frac{1}{A} + \frac{1}{B} e^{-jC} \right) \quad (7)$$

$$\bar{P}_4(j) = \frac{W_1}{W_1 + W_{2,M} + W_{3,M} + +W_{4,M}} \frac{1}{Da_2 Da_3 Da_4} \cdot \frac{1}{C} \bar{P}_1(j) \cdot \left(\left(\frac{B-A}{AB(D-A)} - \frac{1}{AD} + \frac{1}{B(C+D)} \right) e^{Dj} - \frac{1}{A((D-A))} e^{Aj} + \frac{1}{B(D-A)} e^{(B-C)j} + \frac{1}{AD} - \frac{1}{B(C+D)} e^{-jC} \right) \quad (8)$$

A similar volume correction has to be applied to the monomer input concentrations

$$M_{n,in} = \frac{W_n}{W_{mon}} \left(M_{n,0} - M_{n-1,0} \cdot \frac{W_{n-1}}{W_n} + k_p \cdot M_{n,0} \cdot \tau_n \cdot I_{in} \cdot \frac{W_1}{W_n} = \frac{Da_n}{k_p \tau_n} + Da_n \cdot \frac{W_1}{W_n} \cdot I_{in} - \frac{Da_{n-1} W_{n-1}}{k_p \tau_{n-1} W_n} \right)$$

where W_{mon} is the volumetric flow rate of the additional monomer feed stream.

2.2 MWD design with a CSTR cascade

The calculation methodology can be readily reversed. Based on the reversed calculation sequence, a design algorithm has been established in order to predict reactor parameters and feed profiles to meet a target MWD [2, 9]. The concept of the design process is shown in Fig. 1.

Fig. 5. MWD predictions for 4-stage CSTR cascade. Case c) Stage by stage Damköhler numbers are increasing

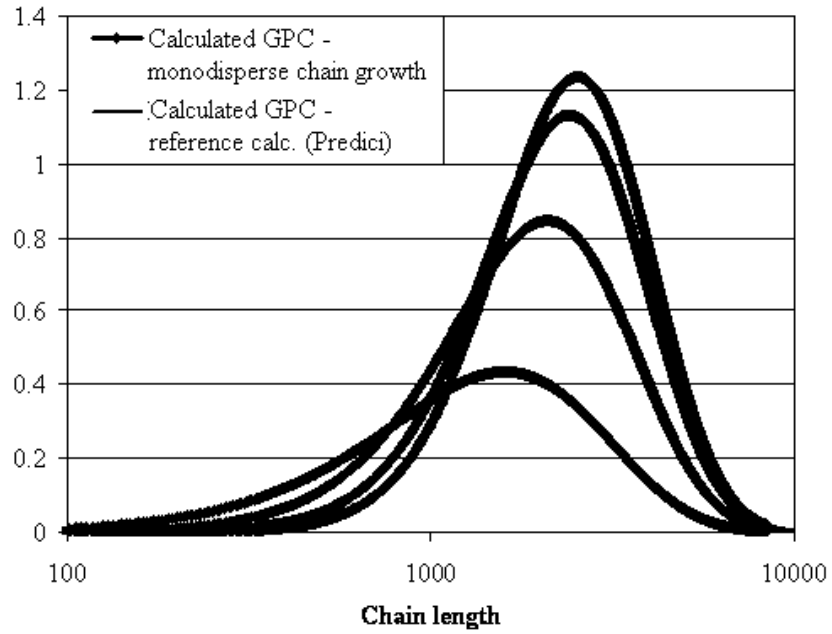
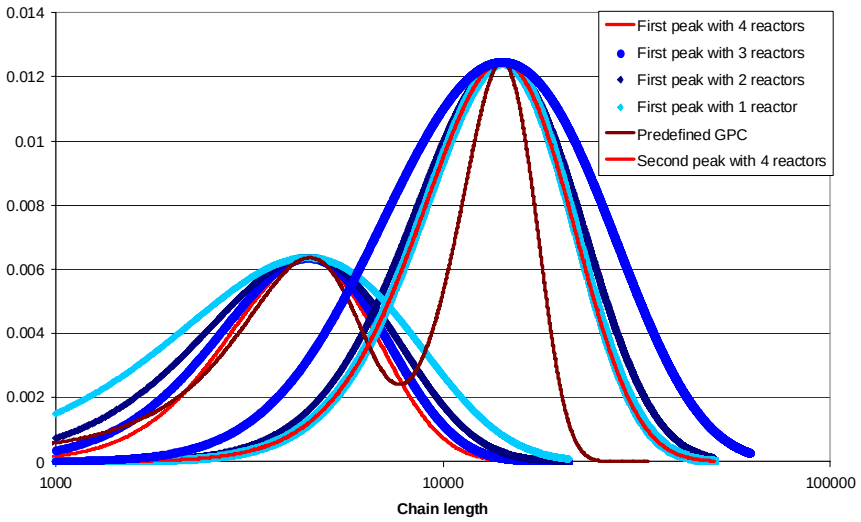


Fig. 6. Component distribution fits for target GPC peaks



The MWD design process is intended to use no other product information apart from the GPC chromatogram of the desired product.

The design parameters to be determined are the number of stages needed, initiator and monomer input concentrations and the Damkohler numbers stage by stage. The Damkohler number lumps together the volumetric flow rate, the reactor temperature and the average residence time which can be specified at a later step of the design process based on practical considerations.

In practice, the number of stages is fixed and, if the feasible MWDs are very far from the desired ones, additional stages will be considered and the design process will be repeated.

It is clear that there are limitations, especially on the minimal possible dispersity of the MWD if a low number of stages are used in the cascade. A batch process is more desirable for a very low dispersity MWD. However, complex, multi-peak distributions are well fitted for our design algorithm.

The target overall MWD is treated as a linear combination of several distributions of predefined type. The components are identified by the position and dispersity index of the individual peaks of the overall MWD. The shortest chains are produced in the last stage, the longest ones go through all the stages. Consequently, the design process starts with the last stage of the cascade and proceeds towards to first one.

The average residence times and the relative magnitude of the Damkohler numbers per stage can be derived from the dispersity indices of the component distributions. The minimal dispersity index in a four stage reactor cascade is 1.25 [3], consequently, if the dispersity index of the target MWD is lower than this limit, identical (i.e. overlapping) component distributions will give the best compromise.

As a general rule, if the individual peaks are well resolved, i.e. their dispersity index is relatively low, the stage Damkohler numbers have to be as close to each other as possible in order to produce a low dispersity peak.

The stage Damkohler numbers are derived from the peak position of the component distributions. The peak position has been calculated from the root of the first derivative of the com-

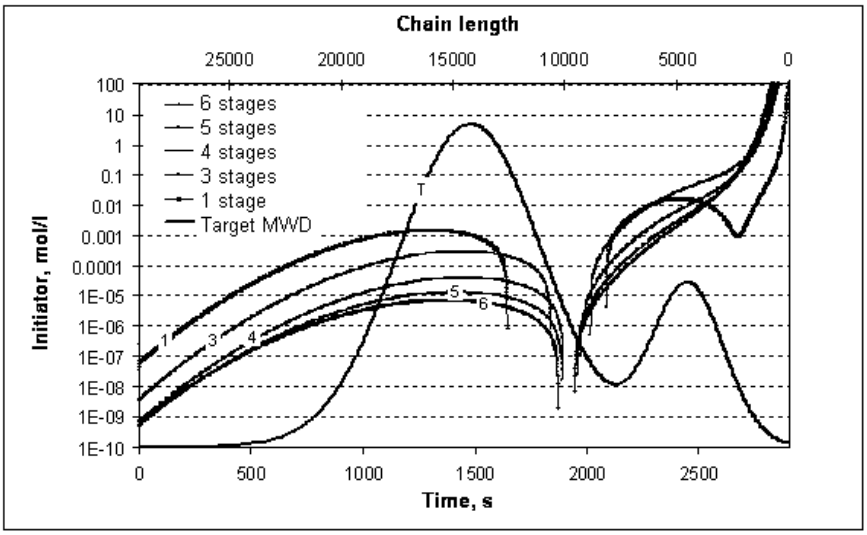


Fig. 7. Predicted initiator input profiles with various number of stages.

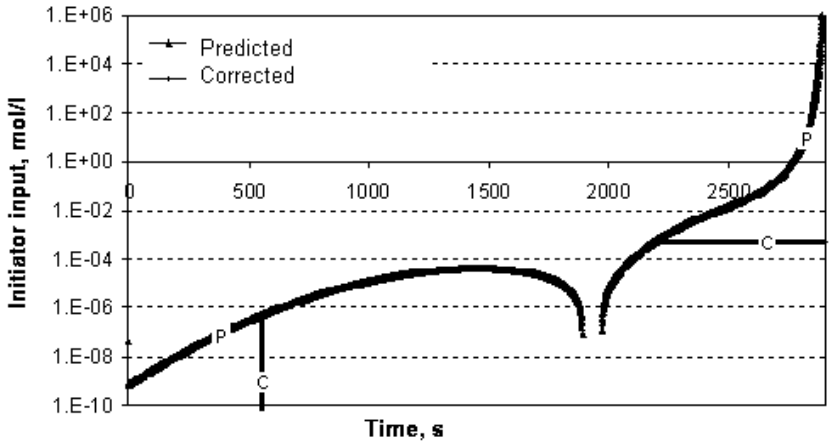


Fig. 8. Predicted initiator input profile with feasibility correction for a 4-stage CSTR.

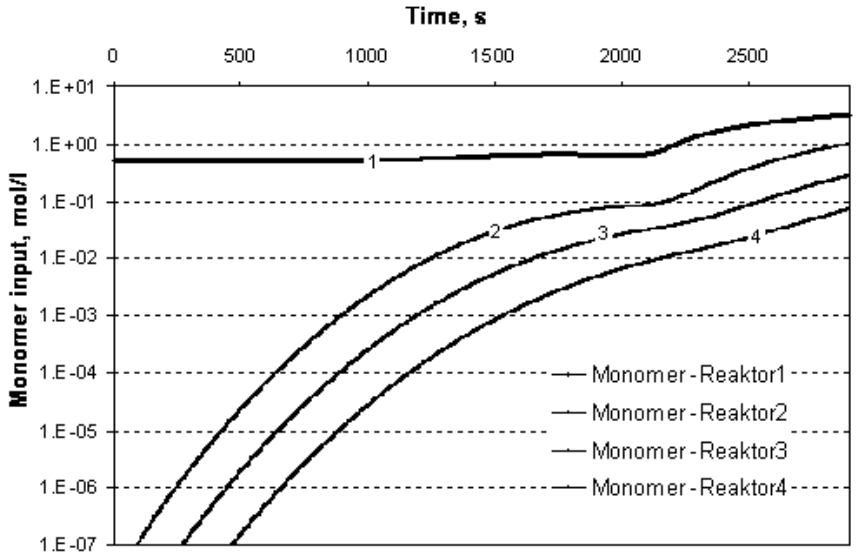


Fig. 9. Predicted stage by stage monomer input profiles for a 4-stage CSTR.

ponent distribution with respect to chain length.

The component distribution is a GPC, i.e. the function to fit is the (above defined) number chain length distribution weighted with chain length squared. Peak position is derived as

$$\frac{dGPC_n(j)}{dj} = \frac{dP_n(j)\cdot j^2}{dj} = 0$$

Carrying out differentiation for the above defined distributions stage by stage:

$$j = \frac{-2}{\ln\left(\frac{Da_1}{Da_1+1}\right)} \qquad n = 1 \tag{9}$$

$$\left(2 - \frac{j}{Da_1+1}\right)e^{-\frac{j}{Da_1+1}} - \left(2 - \frac{j}{Da_2}\right)e^{-\frac{j}{Da_2}} = 0 \quad n = 2 \tag{10}$$

$$\left(\left(1-\frac{A}{B}\right)\cdot e^{Aj}-\frac{C}{B}\cdot e^{-Cj}\right)j+\left(2+\ln\left(\frac{Da_1}{Da_1+1}\right)j\right)$$
$$\left(\left(\frac{1}{A}-\frac{1}{B}\right)\cdot e^{Aj}-\frac{1}{A}+\frac{1}{B}\cdot e^{-Cj}\right)=0\quad n=3 \tag{11}$$

$$\left(\left(\frac{B-A}{AB(D-A)}-\frac{1}{AD}+\frac{1}{B(C+D)}\right)e^{Dj}-\frac{B-A}{AB(D-A)}e^{Aj}+\right.$$
$$\left.+\frac{1}{AD}-\frac{1}{B(C+D)}e^{-jC}\right)\left(2+j\ln\left(\frac{Da_1}{Da_1+1}\right)\right)+$$
$$+\left(\left(\frac{B-A}{AB(D-A)}-\frac{1}{AD}+\frac{1}{B(C+D)}\right)\right.$$
$$\left.De^{Dj}-\frac{B-A}{B(D-A)}e^{Aj}+\frac{C}{B(C+D)}e^{-jC}\right)j=0\quad n=4 \tag{12}$$

It is evident that the number of stages in the cascade has to be greater or equal to the number of peaks in the GPC. Each peak needs a separate initiator input to a certain stage. However, if more stages are available than peaks, several assignments are possible for initiator inputs.

As it has been already mentioned, the process parameters are calculated working from the last stage towards the first one. If there are m peaks in the GPC and n stages are available (n >= m), theoretically, there are n-m+1 possibilities to assign stages to the first peak (shortest chains) of the GPC, i.e. the sets [n], [n-1, n], [n-2, n-1, n] ... [n-m+1, n-m+2, ... n] are feasible choices. The corresponding monomer input concentration and Damkohler number can be obtained by solving Equations (3-5). The initiator input concentration can be derived from the GPC peak area.

Repeating the procedure for the second and further peaks of the GPC, the results can be summarised in a tree graph or a table, listing all possible stage assignments to peaks. An example for 2 peaks and 4 stages is shown in Table 1.

Tab. 1. Possible cascade stage assignments to GPC peaks. Bimodal target GPC, 4-stage CSTR.

Assigned stages to 1^{st} peak	Assigned stages to 2^{nd} peak	Initiator input to stages
4	1, 2, 3, 4	1, 4
3, 4	1, 2, 3, 4	1, 3
2, 3, 4	1, 2, 3, 4	1, 2

Since both the derivation of the process parameters for each of the choices and the prediction of the final GPC is a relatively easy task, all the cases can be evaluated and compared, and the case best fitting the target MWD can be selected.

2.3 MWD prediction and design with an unsteady CSTR cascade

Central to our methodology is the idea that the approximated MWD should be calculated with an explicit formula instead of solving a large set of equations. The main simplification has been the assumption of monodisperse growth.

For design calculations in a CSTR cascade, in order to easily invert the MWD prediction formula, the assumption of steady state operation has been used in the previous sections. Alternatively, if both the stage by stage average residence times and the Damkohler numbers are uniform, explicit and invertible MWD prediction and design formulas can be derived for unsteady operation of a CSTR cascade.

The overall residence time distribution (RTD) of an n-stage CSTR cascade with uniform stage by stage average residence times is [8]:

$$E\left(t_{end}-t\right)=\frac{n^n}{(n-1)!}\cdot\left(\frac{t_{end}-t}{\tau_{cascade}}\right)^{n-1}e^{-n\cdot\frac{t_{end}-t}{\tau_{cascade}}} \tag{13}$$

where $\tau_{cascade}$ is the overall average residence time:

$$\tau_{cascade}=n\cdot\tau$$

Since initiation is assumed to be instantaneous, and the dispersion caused by chain propagation is neglected, the polydispersity index of the MWD is defined by the variance of the residence time distribution function [5]. The variance of the RTD in terms of reduced time is [8]:

$$D_n-1=\sigma^2\left(t_r\right)=\int_0^\infty\left(t_r-1\right)^2E\left(t_r\right)dt_r=\frac{1}{n}\text{ where }t_r=\frac{t}{\tau_{cascade}}$$

$$D_n=1+\frac{1}{n} \tag{14}$$

As it is known, the behaviour of the CSTR cascade tends to that of the plug flow reactor as n is increased.

The NCLD of the product from the cascade is derived by substituting Equation (8) into the general NCLD prediction formula of the method of monodisperse growth [9]:

$$P_j(t_{end})=\int_{t=t_0}^{t_{end}}\delta\left[j-\left(\mu(t_{end})-\mu(t)\right)\right]\cdot$$

$$\cdot\frac{n^n}{(n-1)!}\cdot\left(\frac{t_{end}-t}{\tau_{kaszkad}}\right)^{n-1}e^{-n\cdot\frac{t_{end}-t}{\tau_{kaszkad}}}\cdot\frac{I_{in}(t)}{\tau_{kaszkad}}dt$$

The integration is carried out in a manner similar to that in Section 2.1. After integration the instantaneous NCLD is given as an explicit function of the input initiator profile:

$$P_j(t)=\frac{n^n}{(n-1)!}\cdot\left(\frac{j+1}{n\cdot Da}\right)^{n-1}e^{-\cdot\frac{j-1}{Da}}\cdot$$
$$\frac{1}{\tau_{kaszkad}\cdot k_pM_0}\cdot I_{in}\left(t-\frac{j-1}{k_pM_0}\right)$$

Consequently, the time-averaged NCLD is a function of the integral of the initiator input profile. It is emphasized that only a single integration is needed to calculate a full distribution in any detail.

$$\overline{P_j}(t_{end})=\frac{1}{t_{end}}\cdot\frac{1}{n\cdot Da}\cdot\frac{n^n}{(n-1)!}\cdot$$
$$\left(\frac{j+1}{n\cdot Da}\right)^{n-1}e^{-\frac{j-1}{Da}}\cdot\int_{t=0}^{t_{end}-(j-1)/\left(k_pM_0\right)}I_{in}\left(t\right)dt \tag{15}$$

The inversion procedure of Eq. (10), in order to derive the MWD design formula, is exactly the same as detailed earlier [9] apart from set of different factors coming from the RTD:

$$I_{in}\left(t_{end}-\frac{j-1}{k_p M_0}\right)=\tau_{kaszkad}k_p M_0\cdot\frac{(n-1)\ !}{n^n}\frac{\partial F_j\left(t_{end}\right)}{\partial j}$$

where

$$F_j\left(t\right)=\left(j_{\max}-1\right)\cdot\left(\frac{j+1}{n\cdot Da}\right)^{1-n}\cdot e^{\frac{j-1}{Da}}\cdot\overline{P}_j\left(t\right)$$

The stage by stage monomer input profiles, needed to maintain a constant monomer level, are derived from the monomer component balance equations. For stage 1:

$$M_{1,in}\left(t\right)=M_0+I_{in}\left(t\right)+k_p\cdot M_0\cdot P_1\left(t\right)\qquad(16)$$

where

$$P_1\left(t\right)=\int_{\theta=0}^{t}I_{in}\left(\theta\right)\cdot e^{-\frac{t-\theta}{\tau}}d\theta$$

For the rest of the stages, i.e. for $n > 1$:

$$M_{n,in}\left(t\right)=k_p\cdot M_0\cdot P_n\left(t\right)=k_p\cdot M_0\int_{\theta=0}^{t}P_{n-1}\left(\theta\right)\cdot e^{-\frac{t-\theta}{\tau}}d\theta\qquad(17)$$

3 Results and Discussion

3.1 MWD prediction for a steady state CSTR cascade

The simplified MWD prediction method of monodisperse growth has been used in several examples. The cases form a study to demonstrate the effect of the distribution of chain growth in the various stages on the dispersity index, D_n. As it has been shown, average chain growth is defined by the Damköhler number.

Three Cases are reported. In Case A stage by stage Damköhler numbers are (nearly) identical, the 0.001% differences are due to numerical reasons. In Case B the Damköhler numbers increase, in Case C they decrease with Da, as it is shown in Table 2. In all Cases the desired overall average chain length, μ_n is identical ($Da_{overall} = 2000$).

Tab. 2. Stage by stage Damköhler numbers

	Stage-1	Stage-2	Stage-3	Stage-4
Case A	500.001	500.002	500.003	500.004
B	200	400	600	800
C	800	600	400	200

All calculations have been checked against and in the Figures the computed distributions are shown together with the results of a reference MDW calculation method, i.e. MWDs obtained with the commercial Predici package (Wulkow, 1993; Wulkow, 1996). The differences are negligible, the curves are identical in all cases.

Tab. 3. MWD prediction for a 4-stage CSTR cascade.

Parameter	Common value in all cases
W_1	0,1 [l/s]
$V_1 = V_2 = V_3 = V_4$	40 [l]
$W_{2,Mon} = W_{3,Mon} = W_{4,Mon}$	0,001 [l/s]
k_p	20 [l/mol/s]
I_{in}	0,001 [mol/l]

The flow rates, concentrations and other particular parameters used in Cases A, B, C are summarized in Tables 3 and 4. It has been assumed that all stages have equal volume, V_n, and the reaction is isothermal.

The resulting MWDs are shown in Figs. 3-5. It can be seen that the predictions from Eqs. (1,6-8) are identical to the reference curves. It is remarkable, since Eqs. (1,6-8) are explicit formulas, while the reference method requires the solution of a large set of equations.

The average chain length and the dispersity index of the MDWs are shown in Table 5 for all the above Cases. The differences between the method of monodisperse growth and the reference results (Predici) are less than 1% in all Cases.

3.2 MWD design with a CSTR cascade

The method described in Section 2.2 has been applied to a bimodal target GPC (Fig. 6) with peak positions of j = 4480 és a j = 14200 in terms of chain length. Consequently, two component distributions are needed.

The target GPC is to be produced in a 4-stage CSTR cascade. For the assignment calculations of the second initiator feed to the possible stages, it is assumed that the Damkohler numbers of stages assigned to a peak are identical, since this is the best strategy for a low dispersity component distribution.

In order to fit the position of the first peak of the GPC with a component distribution Equations (9-12) have been solved for stage Damkohler numbers. The solution has been calculated with the Solver Add-in of MS Excel and the results are shown in Fig. 6 and Table 6.

Assigning x stages to the first peak, 4-x stage Damkohler numbers remain to fit the second peak. For cases (4-x) > 1 identical stage Damkohler numbers have been used in order to obtain a lower dispersity component distribution. The results are shown in Fig. 6 and Table 7. For fitting the second component distribution the previously fixed Damkohler numbers are used as constraints (shown in gray in Table 7).

It can be seen in Fig. 6 that four stages give the best fit (lowest dispersity), however, the maximum number of stages that can be assigned to the first peak of the target GPC is 3 (stages 2, 3, 4).

It can be seen in Fig. 6 that the polydispersity of all the calculated distributions are bigger than that of the target (D_n = 1.05). It has been shown previously that the minimal feasible polydispersity for a 4-stage CSTR is 1.25, see Equation (9). Distributions matching the polydispersity of the target GPC are feasible

Tab. 4. MWD prediction for a 4-stage CSTR cascade. Stage by stage Damköhler numbers are A) constant, B) increasing, C) decreasing

A							
Da_1	500		Da_2	500,01	Da_3	500,02	Da_4	500,03
Tau_1	400	s	Tau_2	363,64	Tau_3	333,33	Tau_4	307,69
Mo_1	0,0625	mol/l	Mo_2	0,0688	Mo_3	0,0750	Mo_4	0,0813
M_{in1}	5,6350	mol/l	M_{in2}	5,1314	M_{in3}	5,1440	M_{in4}	5,1566
W_1	0,1	l/s	W_2	0,11	W_3	0,12	W_4	0,13
B							
Da1	200		Da_2	400	Da_3	600	Da_4	800
Tau_1	400	sec	Tau_2	363,64	Tau_3	333,33	Tau_4	307,69
Mo_1	0,025	mol/l	Mo_2	0,055	Mo_3	0,09	Mo_4	0,13
M_{in1}	2,2600	mol/l	M_{in2}	4,3550	M_{in3}	6,4750	M_{in4}	8,6100
W_1	0,1	l/s	W_2	0,11	W_3	0,12	W_4	0,13
C							
Da1	800		Da_2	600	Da_3	400	Da_4	200
Tau_1	400	s	Tau_2	363,64	Tau_3	333,33	Tau_4	307,69
Mo_1	0,1	mol/l	Mo_2	0,0825	Mo_3	0,06	Mo_4	0,0325
M_{in1}	9,0100	mol/l	M_{in2}	5,9075	M_{in3}	3,8125	M_{in4}	1,7025
W_1	0,1	l/s	W_2	0,11	W_3	0,12	W_4	0,13

Tab. 5. Parameters of MWD predictions for a 4-stage CSTR cascade. Stage by stage chain lengths and dispersity indices

		Stage-1	**Stage-2**	**Stage-3**	**Stage-4**
	Da	500.001	500.002	500.003	500.004
	D_n	2,00398	1,499956	1,33317	1,24953
Case A	$D_{n,Predici}$	2,00155	1,49834	1,33285	1,24999
	μ_n	499,50	1000,00	1500,97	2001,74
	$\mu_{n,\mathrm{Pr}edici}$	498,312	1000,642	1500,731	2000,82
	Da	200	400	600	800
	D_n	2,00995	1,55446	1,38839	1,29819
B	$D_{n,Predici}$	1,99872	1,55434	1,38932	1,30008
	μ_n	199,51	598,52	1200,97	2015,03
	$\mu_{n,\mathrm{Pr}edici}$	199,92	600,85	1200,89	2000,96
	Da	800	600	400	200
	D_n	2,00013	1,50767	1,35528	1,29717
C	$D_{n,Predici}$	2,00246	1,50948	1,35815	1,30017
	μ_n	799,28	1399,42	1799,49	1999,11
	$\mu_{n,\mathrm{Pr}edici}$	796,61	1400,76	1800,89	2000,87

Tab. 6. Stage by stage Damkohler numbers for a component distribution fitted to the first peak of the target GPC

Peak 1 fitted with	Stage 1	Stage 2	Stage 3	Stage 4
a.) 4 stages	896	896	896	896
b.) 3 stages	-	**1120**	**1120**	**1120**
c.) 2 stages	-	-	1493	1493
d.) 1 stage	-	-	-	2240

in cascades with 20 or more stages only.

It is obvious that the choice of the best overall fit is a trade-off between the fits of the individual peaks. If no other factors are taken into account apart from the dispersity index, case c) seems to be the best fit, i.e. introducing the second initiator input to the third stage.

Tab. 7. Stage by stage Damkohler numbers. Fits to both peaks of the target GPC.

Peak 1 fitted with	Stage 1	Stage 2	Stage 3	Stage 4
b.) 3 stages	7049	1120	1120	1120
c.) 2 stages	4102	4102	1493	1493
d.) 1 stages	3038	3038	3038	2240

The resulting predicted GPC is shown in Fig. 10 together with the target. The predicted curve is an envelope for the target GPC due to the low number of stages used. In a real situation the design procedure should be repeated with the maximum number of stages desired. Alternatively, the predicted GPC could be calculated for various number of stages, and the predicted overall GPCs could be compared in order to select the number of stages needed.

Having been obtained the stage by stage Damkohler numbers, the monomer input concentration is derived as a function of average residence time in stage and reaction rate constant. The initiator input concentrations are derived from target GPC peak areas. The derived parameters for the chosen case c) are shown in Table 8.

3.3 MWD design with an unsteady CSTR cascade

MWD design calculations have been carried out for the bimodal GPC example of Section 3.2 using assumptions detailed in Section 2.3, i.e. i) single (unsteady) production process, ii) uniform stage by stage average residence times and Damkohler numbers.

The predicted initiator input profiles are shown in Fig. 7 for several total number of stages. In the same graph, on a reversed linear chain length scale according to Eq. (2) the target GPC is shown in NCLD format.

Fig. 10. Target and predicted GPCs

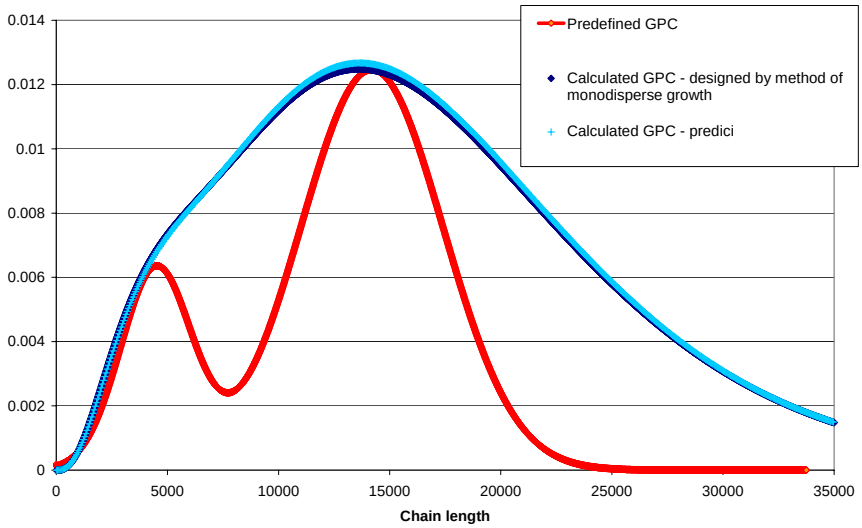


Fig. 11. GPC expected from predicted input profiles.

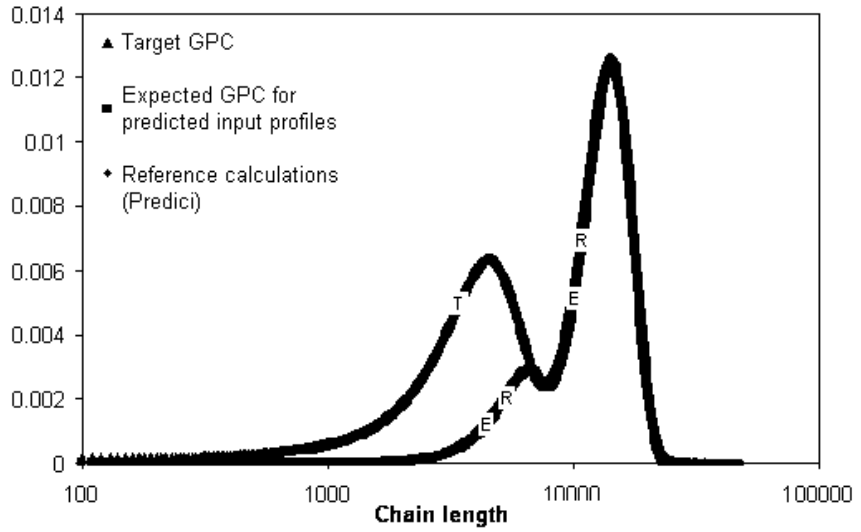
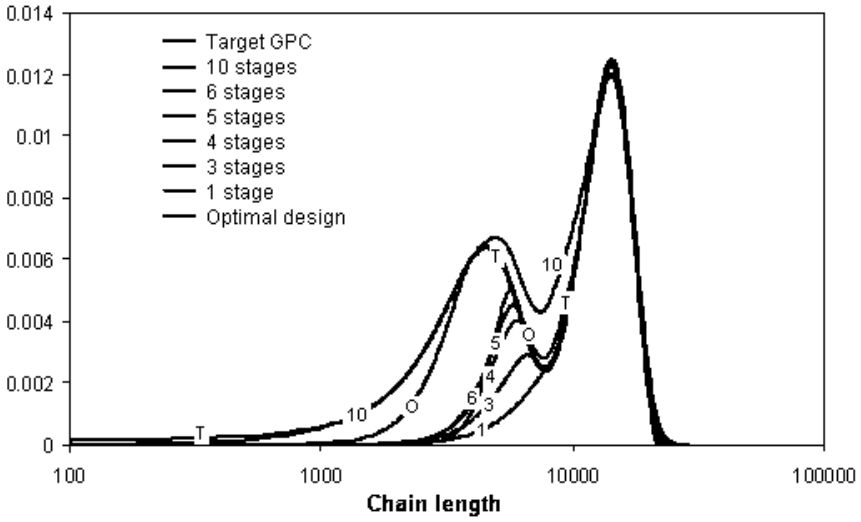


Fig. 12. Expected GPCs from predicted input profiles for various total number of stages.



Note that the narrow second peak of the MWD (on the left) "translates" into profiles with an infeasible section in the 1600-2100 sec range. Here the number of polymer molecules should be decreased in order to produce the required MWD which is not possible with the reaction scheme assumed. In practice, however, a "killing agent" could be applied. This strategy is not considered in this work and is going to be published elsewhere. The infeasible concentration ranges have been substituted with the feasibility limit, i.e. zero initiator concentration.

In can be seen in Fig. 7 that the length of the infeasible range is decreasing as the number of stages is increasing.

For short chains the feasibility limit depends on the highest safe and possible initiator concentration. In practice, a decreased average residence time in the last stage(s) might help. This strat-

Tab. 8. Predicted parameters of a 4-stage CSTR to produce a target GPC

Parameter	Stage 1	Stage 2	Stage 3	Stage 4
Da_i	4102	4102	1493	1493
Tau_i, sec	500	444	267	250
Iin_i, mol/l	2,75E-06		2,80E-06	
Mo_i, mol/l	0,41015	0,46142	0,27991	0,29857
$M_{in,i}$, mol/l	3,37146	0,96180	0,02356	0,67401
V_i, l	40	40	40	40
Stage inp flow rate				
$W_{in,I}$, l/sec	0,08	0,09	0,15	0,16
Monomer input flow rate				
$W_{Mon,I}$, l/sec	0,01	0,01	0,06	0,01

egy is briefly addressed at the end of this section.

For the sake of comparison the predicted initiator input of the 4-stage CSTR cascade has been analyzed. Assumptions for the feasibility limits of the initiator concentration have been:

1 max. initiator concentration is one thousands of the monomer concentration: 5.10^{-4} *mol/l*

2 min. initiator concentration is three orders of magnitude less than max.: 5.10^{-7} *mol/l*

The corrected initiator input profile is shown in Fig. 8.

From the corrected initiator profile the necessary monomer input is derived using Equations (16-17) and shown in Fig. 9. Using the predicted input profiles the product MWD has been calculated with both the method of monodisperse growth and our reference method (Predici) and are shown in Fig. 11.

The GPC expected from the predicted input profiles is nearly identical to the reference calculations (Predici). However, significant deviations from the target GPC can be seen for the short chain region due to the relatively low upper feasibility limit of the initiator input concentration.

Repeating the design procedure with several different number of stages, the expected GPCs are shown in Fig. 12.

It can be seen that 5 stages allow for a better result, but 6 and higher number of stages tend to produce a too narrow first peak. The 1 stage result is good in terms of the high amount of short chains, however, the two peaks overlap much more significantly. The same effects can be identified in Fig. 7 for the predicted initiator profiles.

The shape of the predicted GPC can be "trimmed" in several ways. On of the possibilities is to lower the average residence time in order to produce more short chains and, at the same time increase the monomer concentration for the long chain region to maintain chain length there, see curve in Fig. 12 noted "Optimal design". However, this will shift the position of the first peak towards the shorter chains region, and increase the peak overlap at the same time, too.

In general it is demonstrated that varying the average residence time, the initiator input profile and the total number of stages the best fit can be found as a compromise. Given some sort of object function to define a "good fit" of the target and predicted GPCs, the best parameter set can be derived with an optimization procedure.

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