DYNAMIC SIMULATION AND OPTIMIZATION OF A PLUG-FLOW REACTOR WITHIN THE MINLP SYNTHESIS OF OVERALL PROCESS SCHEMES

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Abstract

This contribution describes the development of a mixed integer nonlinear programming (MINLP) model for a differential non-isothermal plug-flow (PFR) reactor network, based on experience gained when developing a nonlinear programming (NLP) model for batch reactors. Each PFR was modelled as an NLP train of differential segments (final elements) rather than an MINLP train. This model was then applied to a process synthesis example regarding the production of allyl chloride.
In the first step of the NLP model's development, simulation has to be performed in order to analyze the preliminary behaviour of a given kinetic system, and to provide a good initial point for optimization. PFR reactors in the allyl chloride example are currently modelled using mixed-integer nonlinear programming (MINLP) models, where differential-algebraic equations (DAE) are converted into an algebraic system of equations by the use of an Orthogonal Collocation on Finite Element (OCFE), which can be combinatorially very expensive, especially when the reactor network is part of an overall process scheme. The efficiency of MINLP process synthesis can be improved, using the NLP model for the train of differential segments. The length of each final element is then declared as variable, and optimal residence time is shifted to the end of the final element. In this way, some equations become linear and the combinatorics of the model is significantly reduced. This is especially emphasized when the reactor network model is a part of the entire process superstructure. Results show the considerable impact of the decrease in combinatorial burden, nonlinearity, and the effects of nonconvexities, on the efficiency and success of the optimization.

Keywords: PFR reactor, orthogonal collocation, NLP, MINLP, process synthesis.

Presenting Author's biography

Marcel Ropotar. Since 2005 he is a PhD student at the Faculty of Chemistry and Chemical Engineering at the University of Maribor, here he graduated in 2004. He is currently a young researcher and employee of Tanin Sevnica, kemična industrija d.d..

1 Introduction

Recent research to in the optimization of batch and plug-flow reactors could be classified as modelling [1], dynamic optimization [2], [3] and/or on-line optimization [4], [5]. Kinetics in batch and plug-flow (PFR) reactors is described using differential equations. These equations represent complex optimization problems, even in small and simple examples. The use of Orthogonal Collocation on Finite Elements (OCFE) in optimization models of batch or PFR reactors has become a well-established numerical method. The OCFE method with a fixed finite element is the most straightforward and easiest. However, when using fixed finite elements directly it is impossible to explicitly model the optimal length of PFR or neither the retention times of the batch reactors nor the optimal outlet concentrations and conditions. Consequently, the use of flexible finite elements is regarded as a conventional approach for overcoming these difficulties [6]. This model, however, seems to have become more nonlinear because the length of the final element is converted into a variable.

A robust procedure for the dynamic off-line optimization of batch reactors was proposed [7]: in order to decrease nonlinearity a differential-algebraic optimization problem (DAOP) model was initially converted into a robust nonlinear programming (NLP) model by the use of Orthogonal Collocation on a fixed, rather than flexible, Finite Element. In addition, a mixed-integer nonlinear programming (MINLP) model and various strategies for the dynamic optimization of a batch reactor were developed [8] in order to obtain a robust model, suitable for NLP or MINLP synthesis problems. Different schemes for OCFE were studied to increase the robustness of the model.

This paper describes the development of a NLP model for the train of PFR segments, and the application of this model to an allyl chloride example. A comparison between this model and the MINLP model of [9] is also given.

2 NLP model for PFRs

2.1 NLP vs. MINLP

When flexible finite elements were applied to the NLP model of the batch reactor [8] the nonlinearity of the model changed: some additional nonlinearities were introduced because the length of the final element was declared as variable. On the other hand, some nonlinearities vanished because optimal time was moved to the end of the final element and several equations became linear. On average, with flexible final elements, nonlinearities were reduced and CPU time also decreased. Therefore, it is promising that the NLP model would behave better during the process synthesis than the MINLP model, especially because the combinatorics of the model can be significantly reduced and the selection of the final element as in the MINLP model can be avoided.

2.2 Batch reactor case

A NLP model for the train of plug-flow reactor segments was developed based on the robust optimization procedure [7] for a batch reactor. The procedure consists of the following steps:

a) Simulation is useful for the preliminary behavioural analysis of a given kinetic system and to provide a good initial point for NLP.

b) Development of a robust NLP model: a differential-algebraic optimization problem (DAOP) model is converted into a robust NLP model by the use of Orthogonal Collocation on fixed Finite Element (OCFE), where the inner optimal point is modelled continuously by the use of a parallel Legendre polynomial representation.

c) NLP optimization of the batch reactor

The OCFE method was applied to convert the DAOP model.

$$\max P = N_b \cdot \left[\sum_{j \in \text{prod}} C_j \cdot c_j V - \sum_{j \in \text{react}} C_i \cdot c_i V - C_{\text{heat/cool}} \left(\Phi_{\text{preheat/precool}} + \int_0^{t^{\text{opt}}} \mathrm{d}\Phi_{\text{heat/cool}} \mathrm{d}t \right) \right]$$

s.t.

$$\frac{\mathrm{d}c_{\mathrm{r}}}{\mathrm{d}t} = -r_{\mathrm{r}} \;\; \forall \mathrm{r} \in \mathrm{react}\,, \;\; \frac{\mathrm{d}c_{\mathrm{p}}}{\mathrm{d}t} = r_{\mathrm{p}} \;\forall \mathrm{p} \in \mathrm{prod}\,, \;\; t \in \left[0, t^{\mathrm{opt}}\right]$$

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\sum_{\mathrm{p} \in \mathrm{prod}} \frac{\Delta_{\mathrm{r}} H_{\mathrm{p}}}{\rho \cdot c_{\mathrm{p}}} \cdot \left(r_{\mathrm{P}}\right) + \frac{\Phi_{\mathrm{S}}(t)}{V \cdot \rho \cdot c_{\mathrm{P}}}$$

$$\Phi_{\text{preheat/precool}} = (+/-)\rho \cdot V \cdot c_{\mathrm{P}} \cdot \left(T_0 - T_{\mathrm{b}}\right) \qquad \text{(DAOP)}$$

where c_{P}, c_{BP}, c_{R} are concentrations of product, by-product and raw material; V is reactor volume; $\Phi_{\text{preheat/precool}}$ and Φ_{S} are heat flows of preheating/precooling and steam, respectively; T_0 is the temperature at the beginning of reaction, T_{b} is the temperature before preheating/precooling (i.e. 293 K); t_{opt} is the optimal termination time; $\Delta_{\mathrm{r}}H$ is the enthalpy of the reaction; ρ is mixture density, c_{P} is heat capacity and from C_1 to C_5 are cost coefficients for product, raw material, by-product, utility and preheating/cooling, respectively.

Illustrative example:

The model (B-NLP), shown, was obtained for the simple example of a batch reactor (Fig. 1), with the following kinetics for the consecutive reaction A → B → C.

$$\frac{\mathrm{d}c_{\mathrm{A}}}{\mathrm{d}t} = -k_0 \cdot \mathrm{e}^{\frac{-E_{\mathrm{a,A}}}{\mathrm{R} \cdot \mathrm{T}}} \cdot c_{\mathrm{A}}$$

$$\frac{\mathrm{d}c_{\mathrm{B}}}{\mathrm{d}t} = k_0 \cdot \mathrm{e}^{\frac{-E_{\mathrm{a,A}}}{\mathrm{R} \cdot \mathrm{T}}} \cdot c_{\mathrm{A}} - k_0 \cdot \mathrm{e}^{\frac{-E_{\mathrm{a,B}}}{\mathrm{R} \cdot \mathrm{T}}} \cdot c_{\mathrm{B}}$$

$$\frac{\mathrm{d}c_\mathrm{C}}{\mathrm{d}t} = k_0 \cdot \mathrm{e}^{\frac{-E_\mathrm{a,B}}{\mathrm{R}\cdot\mathrm{T}}} \cdot c_\mathrm{B}$$

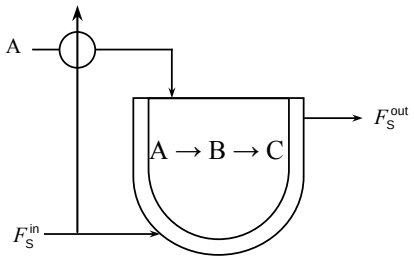


Fig. 1: Batch reactor

A system of differential equations is transformed into an algebraic system of equations. Residuals are included directly into the NLP model as constraints with coefficients, which become decision variables. Collocation points correspond to the shifted roots of an orthogonal Legendre polynomial, and residuals are enforced at the collocation points. Initial and collocation coefficients c_Ai, c_Bi, c_Ci are then used in parallel Legendre polynomials with t^opt as a degree of freedom, in order to define optimal terminal concentrations $c_\mathrm{B}{}^\mathrm{opt}$, $c_\mathrm{C}{}^\mathrm{opt}$ which define revenue in the objective function. Gaussian integration formula $\int_\mathrm{a}^\mathrm{b} f(x)\mathrm{d}x \approx \frac{b-a}{2}\sum_{n=1}^{N} A_n f(x_n)$ was used for approximation of heat consumption integral in the objective function. Note that initial and collocation coefficients for heat flow Φ_S are used in the Gaussian integration.

$$\max_{t^\mathrm{opt},c_\mathrm{A},c_\mathrm{B},c_\mathrm{C},\Phi_\mathrm{preheat},\Phi_\mathrm{S}} Z = \frac{28800}{t_\mathrm{tot}^\mathrm{opt}+600}\cdot\left(\begin{array}{l} C_1 c_{\mathrm{B},l=NE}^\mathrm{opt} V - C_2\cdot c_\mathrm{A}^0 V - C_3\cdot c_{\mathrm{C},l=NE}^\mathrm{opt} V - C_4\cdot\Phi_\mathrm{preheat} - \\ C_5\cdot\sum_{l=1}^{NE}\frac{t_l^\mathrm{opt}}{2}\sum_{n=1}^{N}A_n\sum_{j=1}^{K}\Phi_{\mathrm{S},jl}\cdot\prod_{k=0,k\neq j}^{K}\frac{\frac{t_l^\mathrm{opt}}{2}(x_n+1)-t_{kl}}{t_{jl}-t_{kl}} \end{array}\right)$$

Residual equations and component balances:

$$\left.\begin{array}{l} R_{\mathrm{B},il}(t_{il}) = \sum_{j=0}^{K} c_{\mathrm{B},jl}\cdot\prod_{k=0,k\neq j}^{K}\frac{t_{il}-t_{kl}}{t_{jl}-t_{kl}} - \\ k_0\cdot\mathrm{e}^{\frac{-E_\mathrm{a,A}}{\mathrm{R}\cdot T_{il}}}\cdot c_{\mathrm{A},il} + k_0\cdot\mathrm{e}^{\frac{-E_\mathrm{a,B}}{\mathrm{R}\cdot T_{il}}}\cdot c_{\mathrm{B},il} = 0 \\ R_{\mathrm{C},il}(t_{il}) = \sum_{j=0}^{K} c_{\mathrm{C},jl}\cdot\prod_{k=0,k\neq j}^{K}\frac{t_{il}-t_{kl}}{t_{jl}-t_{kl}} - \\ k_0\cdot\mathrm{e}^{\frac{-E_\mathrm{a,B}}{\mathrm{R}\cdot T_{il}}}\cdot c_{\mathrm{B},il} = 0 \\ \left(c_\mathrm{A}^0 - c_{\mathrm{A},il}\right) = \left(c_{\mathrm{B},il} - c_\mathrm{B}^0\right) + \left(c_{\mathrm{C},il} - c_\mathrm{C}^0\right) \end{array}\right\} \begin{array}{l}\forall i = 1,2,...K \\ \forall l = 1,2,...NE\end{array}$$

Energy balance:

$$\left.\begin{array}{l} R_{T,il}(t_{il}) = \sum_{j=0}^{K} T_{il}\cdot\prod_{k=0,k\neq j}^{K}\frac{t_{il}-t_{kl}}{t_{jl}-t_{kl}} + \frac{\Delta_r H_\mathrm{B}}{\rho\cdot c_p}\cdot \\ \left(k_0\cdot\mathrm{e}^{\frac{-E_\mathrm{a,A}}{\mathrm{R}\cdot T_{il}}}\cdot c_{\mathrm{A},il} - k_0\cdot\mathrm{e}^{\frac{-E_\mathrm{a,B}}{\mathrm{R}\cdot T_{il}}}\cdot c_{\mathrm{B},il}\right) + \\ \frac{\Delta_r H_\mathrm{C}}{\rho\cdot c_\mathrm{p}}\cdot k_0\cdot\mathrm{e}^{\frac{-E_\mathrm{a,B}}{\mathrm{R}\cdot T_{il}}}\cdot c_{\mathrm{B},il} - \frac{\Phi_{\mathrm{S},il}}{V\cdot\rho\cdot c_p} = 0 \end{array}\right\} \begin{array}{l}\forall i = 1,2,...K \\ \forall l = 1,2,...NE\end{array}$$

Optimal outlet point by Legendre polynomials:

$$\left.\begin{array}{l} c_{\mathrm{B},l}^\mathrm{opt}\left(t_l^\mathrm{opt}\right) = \sum_{j=0}^{K} c_{\mathrm{B},jl}\cdot\prod_{k=0,k\neq j}^{K}\frac{t_l^\mathrm{opt}-t_{kl}}{t_{jl}-t_{kl}} \\ T_l^\mathrm{opt}\left(t_l^\mathrm{opt}\right) = \sum_{j=0}^{K} T_{jl}\cdot\prod_{k=0,k\neq j}^{K}\frac{t_l^\mathrm{opt}-t_{kl}}{t_{jl}-t_{kl}} \\ c_{\mathrm{C},l}^\mathrm{opt}\left(t_l^\mathrm{opt}\right) = \sum_{j=0}^{K} c_{\mathrm{C},jl}\cdot\prod_{k=0,k\neq j}^{K}\frac{t_l^\mathrm{opt}-t_{kl}}{t_{jl}-t_{kl}} \\ \Phi_{\mathrm{S},l}^\mathrm{opt}\left(t_l^\mathrm{opt}\right) = \sum_{j=0}^{K} \Phi_{\mathrm{S},jl}\cdot\prod_{k=0,k\neq j}^{K}\frac{t_l^\mathrm{opt}-t_{kl}}{t_{jl}-t_{kl}} \\ c_{\mathrm{A},l}^\mathrm{opt} = c_{\mathrm{A},i=0,l} - \left(c_{\mathrm{B},l}^\mathrm{opt} - c_\mathrm{B}^0\right) - \left(c_{\mathrm{C},l}^\mathrm{opt} - c_\mathrm{C}^0\right) \end{array}\right\} \forall l = 1,2,...NE$$

Initial conditions:

$$c_{\mathrm{A},i=0,l=1} = c_\mathrm{A}^0, \quad c_{\mathrm{B},i=0,l=1} = c_\mathrm{B}^0, \quad c_{\mathrm{C},i=0,l=1} = c_\mathrm{C}^0$$

The point at the interior knot is defined as the optimal interior point from the previous finite element defined by Legendre polynomials:

$$\left.\begin{array}{ll} c_{\mathrm{A},i=0,l} = c_{\mathrm{A},l-1}^\mathrm{opt} & T_{i=0,l} = T_{l-1}^\mathrm{opt} \\ c_{\mathrm{B},i=0,l} = c_{\mathrm{B},l-1}^\mathrm{opt} & \Phi_{\mathrm{S},i=0,l} = \Phi_{\mathrm{S},l-1}^\mathrm{opt} \\ c_{\mathrm{C},i=0,l} = c_{\mathrm{C},l-1}^\mathrm{opt} & \end{array}\right\} \forall l = 2,3,...NE \qquad \text{(B-NLP)}$$

2.3 Development of a NLP model for PFR train

A NLP model for the train of differential non-isothermal segments was developed based on the model (B-NLP) for batch reactors. Both models are very similar except that the batch reactor is integrated over time and PFR over the length of the reactor. Therefore, development of a model for PFR train from the model for a batch reactor was quite straightforward. In the use of the above-illustrative example, a NLP model with flexible final elements for PFR train (P-NLP) is given:

$$\max_{t^\mathrm{opt},c_\mathrm{A},c_\mathrm{B},c_\mathrm{C},\Phi_\mathrm{preheat},\Phi_\mathrm{S}} Z = \frac{28800}{t_\mathrm{tot}^\mathrm{opt}+600}\cdot\left(\begin{array}{l} C_1 c_{\mathrm{B},l=NE}^\mathrm{opt} V - C_2\cdot c_\mathrm{A}^0 V - C_3\cdot c_{\mathrm{C},l=NE}^\mathrm{opt} V - C_4\cdot\Phi_\mathrm{preheat} - \\ C_5\cdot\sum_{l=1}^{NE}\frac{\Delta\alpha_l}{2}\sum_{n=1}^{N}A_n\sum_{j=1}^{K}\Phi_{\mathrm{S},jl}\cdot\prod_{k=0,k\neq j}^{K}\frac{\frac{1}{2}(x_n+1)-t_k}{t_j-t_k} \end{array}\right)$$

Residual equations and component balances:

$$\left.\begin{array}{l} R_{\mathrm{B},il}(t_{il}) = \sum_{j=0}^{K} c_{\mathrm{B},jl}\cdot\prod_{k=0,k\neq j}^{K}\frac{t_{il}-t_{kl}}{t_{jl}-t_{kl}} - \\ k_0\cdot\mathrm{e}^{\frac{-E_\mathrm{a,A}}{\mathrm{R}\cdot T_{il}}}\cdot c_{\mathrm{A},il} + k_0\cdot\mathrm{e}^{\frac{-E_\mathrm{a,B}}{\mathrm{R}\cdot T_{il}}}\cdot c_{\mathrm{B},il} = 0 \\ R_{\mathrm{C},il}(t_{il}) = \sum_{j=0}^{K} c_{\mathrm{C},jl}\cdot\prod_{k=0,k\neq j}^{K}\frac{t_{il}-t_{kl}}{t_{jl}-t_{kl}} - \\ k_0\cdot\mathrm{e}^{\frac{-E_\mathrm{a,B}}{\mathrm{R}\cdot T_{il}}}\cdot c_{\mathrm{B},il} = 0 \\ \left(c_\mathrm{A}^0 - c_{\mathrm{A},il}\right) = \left(c_{\mathrm{B},il} - c_\mathrm{B}^0\right) + \left(c_{\mathrm{C},il} - c_\mathrm{C}^0\right) \end{array}\right\} \begin{array}{l}\forall i = 1,2,...K \\ \forall l = 1,2,...NE\end{array}$$

Energy balance:

$$\left.\begin{aligned} &R_{T,il}(t_{il}) = \sum_{j=0}^{K} T_{il} \cdot \prod_{k=0,k\neq j}^{K} \frac{t_{il}-t_{kl}}{t_{jl}-t_{kl}} + \frac{\Delta_r H_{\mathrm{B}}}{\rho \cdot c_p} \cdot \\ &\left(k_0 \cdot \mathrm{e}^{\frac{-E_{\mathrm{a,A}}}{\mathrm{R}\cdot T_{il}}} \cdot c_{\mathrm{A},il} - k_0 \cdot \mathrm{e}^{\frac{-E_{\mathrm{a,B}}}{\mathrm{R}\cdot T_{il}}} \cdot c_{\mathrm{B},il} \right) + \\ &\frac{\Delta_r H_{\mathrm{C}}}{\rho \cdot c_{\mathrm{p}}} \cdot k_0 \cdot \mathrm{e}^{\frac{-E_{\mathrm{a,B}}}{\mathrm{R}\cdot T_{il}}} \cdot c_{\mathrm{B},il} - \frac{\Phi_{\mathrm{S},il}}{V \cdot \rho \cdot c_p} = 0 \end{aligned}\right\} \begin{aligned} &\forall i = 1,2,...K \\ &\forall l = 1.2....NE \end{aligned}$$

Optimal outlet point by Legendre polynomials:

$$\left.\begin{aligned} c_{\mathrm{B},l}^{\mathrm{opt}}\left(t_l^{\mathrm{opt}}\right) &= \sum_{j=0}^{K} c_{\mathrm{B},jl} \cdot \prod_{k=0,k\neq j}^{K} \frac{1-t_k}{t_j-t_k} \\ T_l^{\mathrm{opt}}\left(t_l^{\mathrm{opt}}\right) &= \sum_{j=0}^{K} T_{jl} \cdot \prod_{k=0,k\neq j}^{K} \frac{1-t_k}{t_j-t_k} \\ c_{\mathrm{C},l}^{\mathrm{opt}}\left(t_l^{\mathrm{opt}}\right) &= \sum_{j=0}^{K} c_{\mathrm{C},jl} \cdot \prod_{k=0,k\neq j}^{K} \frac{1-t_k}{t_j-t_k} \\ \Phi_{\mathrm{S},l}^{\mathrm{opt}}\left(t_l^{\mathrm{opt}}\right) &= \sum_{j=0}^{K} \Phi_{\mathrm{S},jl} \cdot \prod_{k=0,k\neq j}^{K} \frac{1-t_k}{t_j-t_k} \\ c_{\mathrm{A},l}^{\mathrm{opt}} &= c_{\mathrm{A},i=0,l} - \left(c_{\mathrm{B},l}^{\mathrm{opt}} - c_{\mathrm{B}}^{0}\right) - \left(c_{\mathrm{C},l}^{\mathrm{opt}} - c_{\mathrm{C}}^{0}\right) \end{aligned}\right\} \forall l = 1,2,...NE$$

Initial conditions:

$$c_{\mathrm{A},i=0,l=1} = c_{\mathrm{A}}^{0}, \quad c_{\mathrm{B},i=0,l=1} = c_{\mathrm{B}}^{0}, \quad c_{\mathrm{C},i=0,l=1} = c_{\mathrm{C}}^{0}$$

The point at the interior knot is defined as the optimal point from the previous finite element defined by Legendre polynomials at the end point of the final element:

$$\left.\begin{aligned} c_{\mathrm{A},i=0,l} &= c_{\mathrm{A},l-1}^{\mathrm{opt}} \qquad T_{i=0,l} = T_{l-1}^{\mathrm{opt}} \\ c_{\mathrm{B},i=0,l} &= c_{\mathrm{B},l-1}^{\mathrm{opt}} \qquad \Phi_{\mathrm{S},i=0,l} = \Phi_{\mathrm{S},l-1}^{\mathrm{opt}} \\ c_{\mathrm{C},i=0,l} &= c_{\mathrm{C},l-1}^{\mathrm{opt}} \end{aligned}\right\} \forall l = 2,3,...NE \qquad \text{(P-NLP)}$$

It should be noted that the MINLP model is similar to the NLP with the exception of some additional constraints. These are applied in order to select the optimal number of finite elements:

$$y_l \le y_{l-1} \quad \forall l \in \mathrm{NE} \tag{1}$$

$$t_l^{\mathrm{opt}} \le t_l^{\mathrm{opt,UP}} \cdot y_l \tag{2}$$

$$t_l^{\mathrm{opt}} \le t_l^{\mathrm{opt,UP}} + t^{\max} \cdot \left(1-y_l\right) + t^{\max} \cdot \left(1-y_{l+1}\right) \tag{3}$$

$$t_l^{\mathrm{opt}} \ge t_l^{\mathrm{opt,UP}} - t^{\max} \cdot \left(1-y_l\right) - t^{\max} \cdot \left(1-y_{l+1}\right) \tag{4}$$

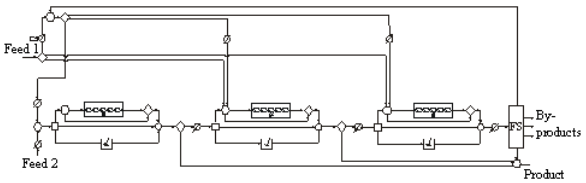
Eq. (1) is applied to ensure that all finite elements up to the last selected one are selected. If the corresponding finite element is rejected, Eq. (2) forces optimal time or the length of the segment to zero. When the finite element is not the last one, Eqs. (3)-(4) are applied to force the t_l^{opt} or l_l^{opt} of each finite element into the upper bound. Hence, all the selected finite elements are fully exploited for integration, except the last one where the optimal time is continuously defined by the Legendre polynomial between the bounds. Note that, in contrast to the NLP model where the integration is distributed equally and continuously within all the finite elements, here integration is applied only to the selected finite elements.

The final step was to apply this model to the process synthesis example of allyl chloride which was solved using a mixed integer process synthesizer MIPSYN (Mixed-Integer Process SYNthesizer), the successor of PROSYN-MINLP [10]. MIPSYN enables automated execution of simultaneous topology, and parameter optimization of the processes.

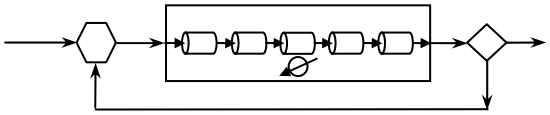
Optimization of each NLP subproblem is performed only on the existing units rather than on the entire superstructure, which substantially reduces the size of the NLP subproblems. The effects of nonconvexities that arise in nonlinear process models are handled by the use of several strategies, which represent an extension of the modeling/decomposition strategy and the AP/OA/ER algorithm. An NLP initializer, model generator and a comprehensive library of models for basic process units and interconnection nodes, together with a comprehensive library of basic physical properties for the most common chemical components were developed in order to facilitate different types of computation (for example initialization, optimizing fixed structures).

3 Allyl chloride example

Process systems where reactors are part of the overall process scheme are numerically difficult to solve. The MINLP model formulation for PFR trains was recently used in an allyl chloride example, as described in [9]. The reactor/separator superstructure (Fig. 2a) comprises a sequence of PFR/CSTRs with side streams and intermediate separators at different locations. Each PFR consists of a train (Fig. 2b) of several differential non-isothermal elements. The optimal number of elements is selected during MINLP optimization.



a)



b)

Fig. 2: a) Superstructure of allyl chloride problem. b) Train of differential segments in PFR.

The corresponding DAE system is modelled by orthogonal collocation on flexible finite elements. Simultaneous heat integration is performed by a Yee's model [11]. The overall model is highly nonlinear and nonconvex. Based on experiences gained by solving the simple example of a batch reactor [8], nonlinearities could be significantly reduced if an NLP model with flexible final elements is applied, rather than the MINLP model. Hence, the MINLP model for PFR trains was converted to an NLP model with flexible final elements.

Since the optimal length is now located at the end of the final element, some equations became linear and, since the selection of optimal final element is overridden, the combinatorial burden is significantly reduced.

3.1 Results and comparison

Optimization of allyl chloride production was first performed with the MINLP model for PFR trains and then with the NLP model. Tab. 1 shows CPU times for NLP and MILP steps until the 15th major MINLP iteration for MINLP, and for the NLP model of PFR trains.

Tab. 1 Solution statistics of allyl chloride problem.

It.	PRF model / phase	CPU for MINLP, s	CPU for NLP, s
1	NLP	36,903	24,782
	MILP	1,280	2,140
2	NLP	0,094	2,813
	MILP	1,484	4,531
3	NLP	1,844	4,078
	MILP	3,171	5,421
4	NLP	2,313	2,531
	MILP	5,842	4,812
5	NLP	1,512	2,113
	MILP	5,217	8,171
6	NLP	1,031	0,547
	MILP	4,639	7,187
7	NLP	0,594	0,688
	MILP	5,514	7,484
8	NLP	0,516	0,625
	MILP	13,013	5,906
9	NLP	1,391	0,234
	MILP	8,482	7,468
10	NLP	0,422	0,438
	MILP	22,714	5,734
11	NLP	1,813	1,516
	MILP	12,778	4,640
12	NLP	2,625	0,422
	MILP	166,217	6,546
13	NLP	0,359	0,516
	MILP	350,305	7,703
14	NLP	2,063	0,328
	MILP	258,214	4,765
15	NLP	1,016	1,250
	MILP	455,690	5,625
∑	**NLP**	**54,496**	**42,881**
	MILP	**1314,560**	**86,207**

As expected from previous experiences [8], the CPU time needed to solve the NLP model with flexible final elements for PFR trains is significantly lower than the one for the MINLP model. However, as can be seen from Tab. 1, the difference is now unexpectedly large – up to two orders of magnitude. It is interesting to note that, in the case of the NLP model for PFR trains, the CPU times of the MILP phase not increase from iteration to iteration, as in the case of the MILP model. Moreover, a better solution was found (82.253 vs. 81.924), and it was noted that the unpleasant effects of nonconvexities are reduced for an order of magnitude.

4 Conclusions

The main goal of the research described in this contribution is to improve the efficiency of the MINLP synthesis of systems which, besides the algebraic system of equations, contains a differential system of equations.

Former research indicates that declaring final elements flexible and, hence, shifting optimal time or length to the end of the final element, actually increases the efficiency of the search because the combinatorial burden, by the use of the NLP model, is significantly reduced. In this way, Big-M MINLP formulation (Eqs. (1)-(4)) of the optimal finite element selection within the PFR train is now avoided.

Based on the experiences gained with the batch reactor, we have developed an NLP model for PFR train, in order to improve the efficiency of the MINLP synthesis of process flowsheet performed by the use of the process synthesizer MIPSYN. The NLP model of PFR trains was tested on the process synthesis example of allyl chloride production.

The results show a surprising increase in efficiency – for an order of magnitude or even more. A supplementary research is under way in order to further improve the efficiency of the search and to decrease the approximation error of OCFE.

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