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Reactor-Network Synthesis via Flux Profile Analysis

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Abstract

Within the framework of elementary process functions (Freund and Sundmacher (2008)) an approach is developed to derive reactor-network candidates from the solution of a dynamic optimization of a batch process scheme by analyzing its optimal mass and energy control fluxes. Thereby, any characteristics of the reaction progress can be identified, e.g. benefits from mixing, back-mixing, recycling, heating, cooling, etc. The approach is used to (i) determine the attainable region for the modified, isothermal van-de-Vusse reaction, which matches literature results; and (ii) synthesize reactor-network candidates for the standard, non-isothermal van-de-Vusse reaction, which gives new insights compared to previous results from literature using superstructure optimization approaches. The results indicate how this approach can be used to determine the attainable region of a process and to rationally select candidates for detailed reactor design with, e.g. superstructure optimization. It further closes the gap between dynamic batch optimization and continuous reactor-network synthesis.

1. Introduction

Process systems engineering deals with and develops methods and concepts based on mathematical modeling to design, analyze and optimize processes in chemical, bio-(chemical) and electro-chemical engineering. Main challenges in process development are the synthesis of an optimal processing route to form a specified product in the most economical way and to build a process which is able to approximate this theoretical processing route in the best way. Thereby, one can distinguish between discontinuous and continuous processes. The former are often associated with smaller scale productions like for pharmaceuticals and fine chemicals, while the latter with large scale productions of bulk chemicals. Due to that the design approaches for both kinds of processes are often distinguished as well. However, it would be more generic to identify the potential of different process pathways or realizations without *a priori* restriction to either discontinuous (batch) or continuous process types. The concept of elementary process functions (EPF) [1] allows in particular for that - the analysis of the maximum potential of a process without preliminary restrictions to the structure, the operational mode and/or the units in the optimal process.

1.1 Process development

The development of an optimal process consists, beside of the decision of the operational mode, of several tasks on different hierarchical levels. As illustrated in Fig. 1 the development of a process contains (i) the *process synthesis*, which is subdivided to *reactor-networks synthesis*, *separator-network synthesis* or *heat-exchanger-network synthesis*, and which aims at finding the best configuration/structure of given standard process parts; (ii) the *process design*, which includes the *reactor design*, the *separator design* and the *heat-exchanger design*, and quantifies detailed design aspects of process units within a given configuration; (iii) the *process intensification*, which aims at improving the process by combination of several functionalities or process units in a single unit or an integrated process; and (iv) the *process control*. The latter is not subject of the presented work. Following the functional modules of the EPF methodology introduced in [1], the functionalities of activating, chemical reaction, heat removal and supply, and separation are included. Simple mixing is not a particular part of the process development scheme, since it normally does not require thermodynamic and kinetic modeling leading to complex optimization problems. The preprocessing and product formulation modules are neglected within this overview, because they are assumed to be independent of the reaction-separation tasks, i.e. the reactants and products are assumed to have the desired properties. Albeit the tasks are subdivided in the given scheme, there are several research fields combining several tasks,

e.g. *reactor-separator-network synthesis* (1), *synthesis-design* problems (2), *simultaneous design and control* problems (3), or *heat integration* tasks (4), etc.

Following the multiscale structure of hierarchical levels of a chemical production process introduced by [2], the task of *process synthesis* takes place on the *plant level* combining several units to a whole plant, whereby the task of *process design* is classified within the *process unit level*, combining and manipulating different phases within a process unit to get a detailed design. *Process intensification* and *process control* act on both levels. The *process intensification* on the *plant level* is linked with the integration of several unit operations or functionalities in multifunctional process units such as heat-integrated reactors or reactive separations. On the *process unit level* the *process intensification* deals e.g. with increasing mass or energy transport phenomena and optimizes specific surface areas of the process unit or the interfacial area between phases.

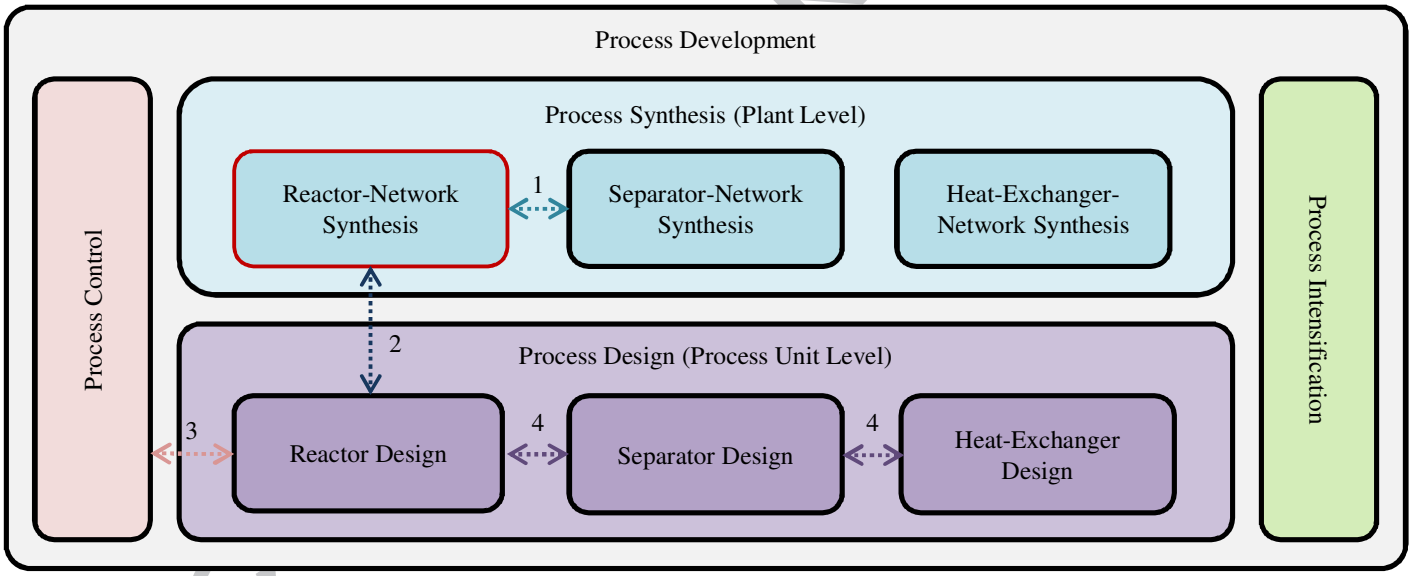


Figure 1: Tasks of process development; red box indicates the application are of this work; (1) *reactor-separator-network synthesis*, (2) *synthesis-design* problems, (3) *simultaneous design and control* problems, or (4) *heat integration* tasks.

Within the framework of elementary process functions a 3-level approach for combined *reactor design* and *process intensification* has been developed in [3]. This approach aims at designing innovative and intensified reactor units, but did not consider the synthesis of networks of reactors with different back-mixing characteristics and recycles inside of this network. This extension is introduced in the presented work, using the basic EPF ideas for the synthesis of reactor-networks.

1.2 Literature Review

First steps for optimal design of chemical reactors already partly based on mathematical programming were conducted in the 1960s, e.g. in [4], [5] and [6]. These studies already emphasized the benefit of dosing of components along the reaction time or the corresponding reactor length to control and increase the selectivities towards desired products.

1.2.1 Synthesis and Design of Batch Reactors

In light of batch process design one has to distinguish between (i) dynamic optimization methods which aim at designing optimal control trajectories for a single batch process and (ii) batch scheduling methods which, in contrast to the dynamic optimization methods, construct a network of various batch processes to explore the maximum potential of a process. A comprehensive overview of dynamic optimization of batch processes accompanied by suitable examples is given in [7]. Batch scheduling approaches are of importance for the design of multipurpose/multiproduct processes of high complexity. In general these approaches apply mixed integer programming techniques either on discretized or continuous time horizons and divide the problem into the individual batch operations (tasks) and the chemical components (states) resulting in a state-task-network. For an introduction and a comprehensive overview the reader is referred to [8] and [9], respectively.

1.2.2 Synthesis and Design of Continuous Reactors

The design of optimal continuous processes is mostly related to reactor-network synthesis. It mainly aims at finding the optimal structure of reactor-networks, their mixing characteristics and residence times, maximizing certain objective function while satisfying the requirements of the overall process. For this task mainly two different approaches are used: the *attainable region* approach and *superstructure optimization.*

The fundamental idea of an attainable region, which contains all sets of points in the concentration space in a chemical process being attainable only by reaction and mixing starting from a given feed point, was introduced by Horn [10]. This approach had its revival in the end of the 1980s, when the idea of attainable regions was developed further by e.g. [11], [12] or [13]. Inter alia, they suggested an approach which allows for graphical construction and interpretation of the attainable region of a process. This method was widely used although it has some drawbacks for higher dimensional systems. Balakrishna and Biegler [14] used this technique to develop a mathematical programming based framework for process design.

The superstructure optimization, originating from a work of Jackson [15], seeks the best reactor-network configuration within a pre-defined superstructure of possible units. The main advantages are that the objective function and the reactor-network are determined simultaneously and that the formulation allows including constraints or changes in e.g. the objective function directly. Main drawback is that the solution can only be part of the pre-defined superstructure. If the best process is not included in the candidate super-structure, it cannot be found. Achenie and Biegler [16,17] used Nonlinear Programming (NLP) techniques to optimize recycle reactors with indirect heat transfer options. Kokossis and Floudas [18] used general structures of PFRs and continuously stirred tank reactors (CSTR), whereby the PFRs were approximated by a cascade of CSTRs with the same volume, and enabled all possible recycling, (intermediate) feeding and by-passing strategies as well as intermediate cooling and heating leading to a large and complex Mixed Integer Nonlinear Programming (MINLP) problem. Further developments in this field are: incorporation of stochastic optimization, e.g. [19]; inclusion of differential side stream reactor (DSR), e.g. [20]; use of optimal control techniques and optimization of cross flow reactors [21]; application of superstructures for attainable region construction using linear programming, e.g. [22]; and numerous applications of these methods for the design of different process examples.

A further interesting work on reactor-network synthesis, which bases as well on an optimal control framework, is the *systematic staging* approach, which was applied to isothermal systems [23] and non-isothermal systems [24].

1.3 Present Work

The framework of the reactor-network synthesis approach, presented in this work, is the dynamic optimization of a special batch process configuration leading to optimal dosing fluxes of all involved components and an optimal heat flux. In contrast to the work of Peschel et al. [3], product dosing is enabled

due to this batch configuration, which is explained in detail in Section 2.1. This extension of the EPF based reactor design allows for:

- Identifying any characteristics of the reaction progress, e.g. advantages of mixing, back-mixing, extraction, by-passing, recycling, heating, cooling, etc., whereby the focus lies on revealing benefits of distributed reactant dosing, back-mixing and recycling by analysis of reactant and product dosing, respectively.
- Determining the attainable region.
- Using the reactor-network candidates obtained from the introduced approach for further superstructure optimizations accounting for e.g. non-idealities and techno-economic aspects.
- Overcoming some drawbacks of the aforementioned state-of-the-art methods, namely the attainable region and superstructure approaches, and closing of the gap between these methods and the dynamic optimization of batch processes.

In the following the methodical background for the reactor-network synthesis approach in the framework of EPF is introduced and the resulting optimization problem is formalized in Section 2. Subsequently, the proposed approach is applied on three examples in Section 3. At first an optimal reactor-network is synthesized for a simple example to ensure that intuitive solutions and well-known reaction engineering phenomena are detected by the proposed design approach and the applied numerical solvers. The second step is related to the identification of the attainable region (AR) of a well-known literature example and the derivation of reactor-network candidates for the optimal point of the AR. The third example aims at directly determining reactor-network candidates, which will be compared to networks given in literature for the same process using superstructure optimization. It follows a discussion of the results and the presented approach in Section 4 and a conclusion in Section 5.

2. Methodical Background

2.1 Methodology of Elementary Process Functions

As mentioned before, the methodical basis of the proposed reactor-network synthesis approach is the method of elementary process functions developed by Freund and Sundmacher [1]. The key idea is a fluid element of arbitrary form which travels through the process and is thereby manipulated optimally by external and internal mass and energy fluxes. This fluid element contains basic information about kinetics and thermodynamic relations describing the essential physico-chemical phenomena in the process. This

information, normally provided in form of mathematical equations, can be divided into states and controllable fluxes, which correspond to nodes and edges in terms of graph theory for reaction networks.

The manipulation of the fluid element states by the acting fluxes intends to make them follow an optimal path in the thermodynamic state space to finally reach a desired optimal point or at least to satisfy or maximize certain objective functions (Fig. 2).

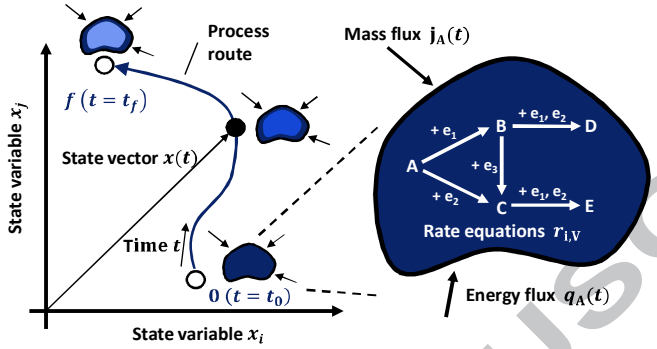


Figure 2: Fluid element in thermodynamic state space (EPF).

Optimizing a process with the EPF method leads to profiles of the external fluxes. These fluxes are mainly of two kinds which both have their particular meaning for process design: (i) mass fluxes which decide about the optimal supply with chemical components adjusting the concentrations; and (ii) energy fluxes which control the temperature level of the process and allow conclusions about heating and cooling strategies. Due to their aforementioned nature as supplier of reactants, mass fluxes contain information about mixing and back-mixing required for an optimal reaction progress. Note, that mass fluxes can as well be negative, meaning an extraction of a species. Taking this additionally into account, one can find an optimal dosing and extraction policy which can be translated into a sequence of reaction, mixing, and separation steps. Thus, the optimal sequence of operations in the process is only depending on the mass fluxes, either dosing or extraction. In this work the focus lies on dosing fluxes and the associated mixing characteristics only. The energy fluxes can be realized independent of the dosing policy in each process step.

2.2 Reactor-Network Synthesis Approach

As mentioned in the introduction, the proposed process synthesis approach intends to find the optimal process independent of the operational mode. If a process is more profitable or efficient in a batch or a continuous plant depends on the reaction itself, the overall process requirements, the particular constraints of the given design problem and/or its objective.

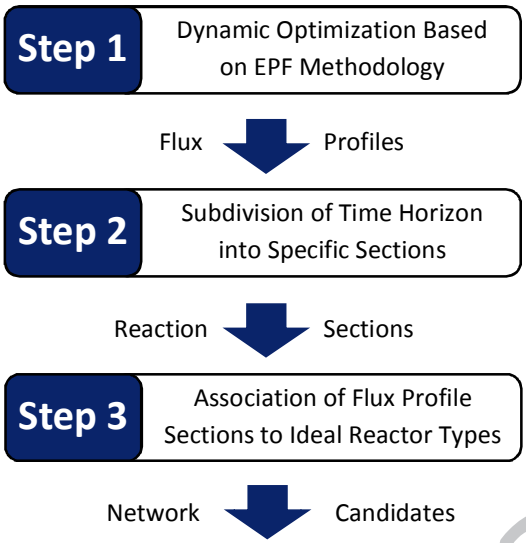


Figure 3: Reactor-Network Synthesis Procedure

Thus, there is a necessity to design a process independently of the operational mode. It should rather be part of the decision-making during technical realization of the optimal process. Albeit aiming at a design approach which is at first independent of the operational mode, the optimization concept introduced in the following is based on a dynamic optimization of a virtual batch process. This perfectly mixed batch process with its feed streams (fed-batch or semi-batch) is analogous to the idea of an arbitrary fluid element with dosing fluxes which is the key concept of the EPF methodology. The reactor-network synthesis or rather the transformation from a batch process to a continuous reactor-network is structured in three steps as depicted in Fig. 3.

2.2.1 Step 1: Dynamic Optimization Based on EPF Methodology

The profiles of the external control fluxes within the EPF methodology are the result of solving a dynamic optimization problem (DOP). The scheme shown in Fig. 4 illustrates the analogous batch process, consisting of a batch process which can be fed from virtual storage tanks containing all involved components, both reactants $(1 \dots N_R)$ and products $(1 \dots N_P)$, and a subsequent ideal separator from which the products are recycled to the corresponding storage tanks. The dosing takes place continuously during the batch reaction time. The separation and the refill of the product tanks is a discontinuous procedure, whereby the separation is assumed to operate ideally so that only pure species are recycled to the storage tanks; otherwise the maximum potential of the process is already reduced by the separation quality. The batch reactor is empty at $t = 0$.

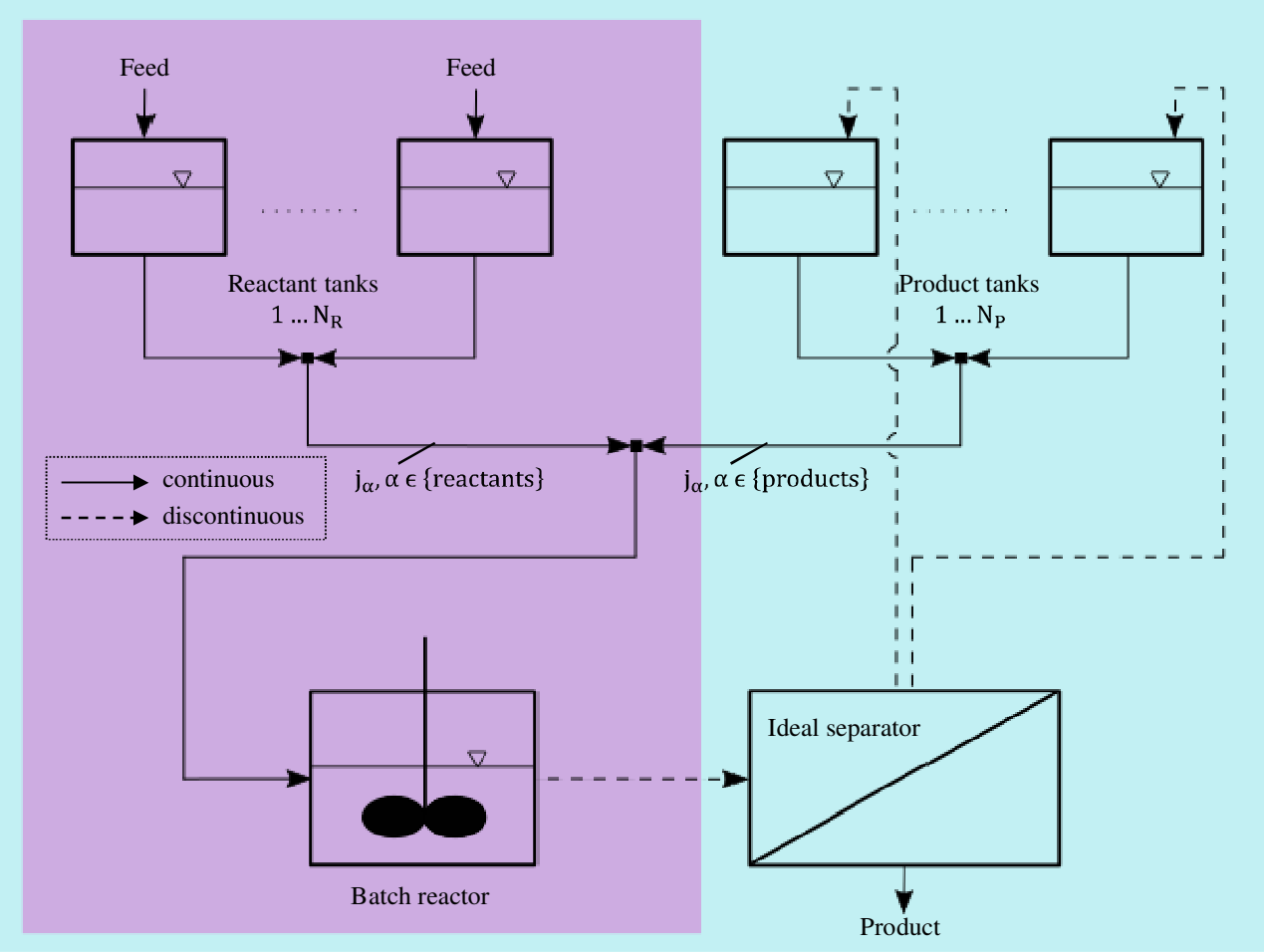


Figure 4: Scheme of batch configuration considered for dynamic optimization corresponding to ideally controlled matter element.

The resulting simple optimization problem has to satisfy the material balance equations for:

$$\frac{dn_\alpha}{dt} = \left(\sum_{m=1}^{M} \nu_{\alpha,m} r_m\right) V_R + j_\alpha(t),\ \forall \alpha \in \{components\}\,, \tag{1}$$

where $\boldsymbol{n} \in \mathbb{R}^N$ are the molar reactor holdups; $\boldsymbol{j} \in \mathbb{R}^N$ are the dosing streams; $\boldsymbol{r} \in \mathbb{R}^M$ are the reaction rates with $\boldsymbol{r} = \boldsymbol{r}(\boldsymbol{c}, T)$ being a function of the component concentrations $\boldsymbol{c}$ and the temperature T; $\nu_{\alpha,m}$ are the stoichiometric coefficients; and V_R is the reaction volume.

Additionally, the storage tank levels are balanced:

$$\frac{dn_{\alpha,st}}{dt} = -j_\alpha(t),\ \forall \alpha \in \{components\}. \tag{2}$$

Since only dosing is considered here, $j_\alpha \geq 0$.

This approach aims at determining the maximum potential of the process and, thus, only the chemical reaction is considered. Any other phenomena such as mass or heat transfer resistances, flow fields, energy dissipation, etc. are neglected, keeping in mind that these non-idealities are decreasing the performance.

Within this framework it is indispensable for the optimization to satisfy certain constraints:

(i) at the end of the process the dosed amount of each product has to be subtracted from the outlet stream to return it to the virtual product tanks which must have the same levels as in the beginning. In this way it is ensured, that no product is dosed just to increase yields and/or selectivities only by dosing:

$$n_\alpha^f = n_\alpha(t_f) - \int_0^{t_f} j_\alpha(t)\, dt,\ \alpha \in \{products\}; \tag{3}$$

(ii) the batch reactor is ideally mixed, no gradients in concentrations or temperature exist. The resulting dynamic optimization problem reads:

$$Obj = \min_{\boldsymbol{j}(t),T(t),t_f} \int_0^{t_f} F(t)dt + I(x_0) + E(x_f)$$

s.t. balance equations: (1) and (2),

products constraint: (3),

with a stage cost $F(t)$, an initial cost $I(x_0)$, and a final cost $E(x_f)$. As result one obtains the final reaction time in the process t_f, the temperature profile $T(t)$ and the vector of dosing flux profiles $\boldsymbol{j}(t)$. The latter two variables are the core of the analysis leading to the optimal series of reactors including sections of back-mixing and recycle benefit. According to the assumption of unlimited heat flux, the temperature represents an energy flux and is thus manipulated directly.

It is important to state that the results of the dynamic optimization of a process in the proposed batch scheme is possibly very sensitive to the bounds of the dosing fluxes and the initial filling level of the storage tanks. Hence, a sensitivity analysis is highly recommended. This is, for instance, the case in the example of Section 3.3, where the by-products dosed at the very beginning of the process are at their upper bounds. Here, increasing the filling levels and thereby the total amount which can be dosed further, improves the optimal process performance.

2.2.2 Step 2: Subdivision of Time Horizon into Specific Sections

Once the dynamic optimization is carried out and the optimal dosing and temperature profiles are determined, one has to subdivide the time horizon of the process into specific sections of characteristic

dosing and heating/cooling behavior. In this step the maximal amount of sections is identified and, thus, translating these sections to a continuous reactor-network would lead to the maximum reactor-network, i.e. the configuration with the maximum reasonable amount of different reaction sections based on the presented approach. How such a subdivision could look like for an arbitrary example of flux profiles is illustrated in Fig. 5. The detailed analysis of the flux profiles is explained later in step 3 of the approach.

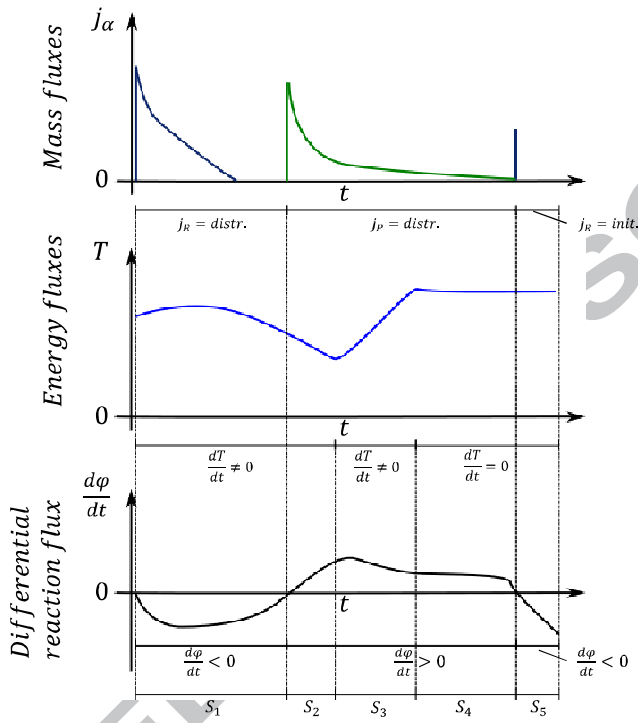


Figure 5: Illustration of subdivision of time horizon of flux profiles. φ – differential selectivity (see Eq. (11)); R – reactant (dark blue); P – product (green).

The following rules have to be complied with:

- The first section starts at $t = 0$ and the last section ends at $t = t_f$.
- Every new dosing of either reactant or product (starting from zero because it was not dosed directly before) indicates a new section.
- A change of temperature between dynamic and constant behavior, and a discontinuity of temperature profile indicates a new section. Temperature changes can indicate impacts of different phenomena, e.g. activation energies, chemical equilibria, solubilities, densities, etc.

In a later step, different sections might be merged again if their realization in a single unit is reasonable.

2.2.3 Step 3: Association of Flux Profile Sections to Ideal Reactor Types

The realization of the control profiles or their specific sections derived in step 2 in a batch process is conceptually trivial. But for the realization of the control fluxes in a continuous process a series of reaction steps with e.g. back-mixing behavior, mixing sections and recycles along the reaction coordinate have to be determined. Hence, the dosing fluxes have to be associated with typical reactor types which can be arranged in a suitable series to approximate the optimal batch dosing profiles. For reactor-network synthesis in reaction engineering the most common ideal reactor concepts, which all have characteristic dosing and mixing properties, are the Plug Flow Reactor (PFR), the Continuously Stirred Tank Reactor (CSTR) and the Differential Sidestream Reactor (DSR). Their characteristic dosing policies can be derived starting from the basic EPF equation:

$$\frac{d\boldsymbol{x}}{dt} = \dot{\boldsymbol{x}} = \sum_{k=1}^{G} g_k(\boldsymbol{x})\, \boldsymbol{e}_k, \tag{4}$$

where $\boldsymbol{x} \in \mathbb{R}^N$ is a vector of arbitrary state variables, $\boldsymbol{g} \in \mathbb{R}^G$ are the control fluxes of the fluid element and $\boldsymbol{e} \in \mathbb{R}^N$ is the basic vector in the thermodynamic state space. As the focus lies on reaction and mixing, the state variables $\boldsymbol{x}$ are replaced by the concentrations $\boldsymbol{c}$. Thus, the basic EPF equation results in a generic mass balance, whereby the control fluxes $\boldsymbol{g}$ are subdivided into internal and external fluxes:

$$\dot{\boldsymbol{c}} = \boldsymbol{N}\boldsymbol{r}(T(t), \boldsymbol{c}(t)) + \boldsymbol{j}_c(t), \tag{5}$$

with $\boldsymbol{N} \in \mathbb{R}^{NxM}$ being the stoichiometric matrix, $\boldsymbol{r}(T(t), \boldsymbol{c}(t)) \in \mathbb{R}^{Mx1}$ being the internal vector of reaction rate fluxes and $\boldsymbol{j}_c(t) \in \mathbb{R}^{Nx1}$ corresponding to the vector of external mass dosing fluxes in units of concentrations. The assumption is made that the heat flux is unlimited and hence can control the temperature of the fluid element perfectly. Since the solution of Eq. (5) results in an initial value problem (IVP), initial conditions are to be specified:

$$\boldsymbol{c}(t = 0) = \boldsymbol{c_0}. \tag{6}$$

From here on one can discuss the three ideal reactor types and derive their characteristic dosing policies and temperature control options.

Differential Sidestream Reactor (DSR): A DSR is such as a PFR back-mixing free, but allows in contrast to the PFR for dosing of components along the reactor length. The balance equation of a DSR corresponds to Eqs. (5)-(6) and allows, thus, for a dynamic control of the dosing fluxes and the temperature. In light of discontinuous processes it can be compared to a fed-batch concept where reactant is dosed to the batch process over time. The residence time τ_f of the DSR corresponds to the reaction time t_f of the fed-batch.

Plug Flow Reactor (PFR): In general, one can derive the PFR balance equation starting from the DSR equations, Eqs. (5)-(6). Assuming the limiting case $\boldsymbol{j}_c(t) = 0$, the only control variables which remain are the initial conditions $\boldsymbol{c}_0$. The resulting IVP reads:

$$\dot{\boldsymbol{c}} = \boldsymbol{N}\boldsymbol{r}(T(t), \boldsymbol{c}(t)), \ with\ \boldsymbol{c}(t = 0) = \boldsymbol{c_0}. \tag{7}$$

Under the assumption that the initial dosing fluxes $\boldsymbol{j}_c(t = 0)$ can realize the initial conditions $\boldsymbol{c_0}$, the dosing policy, in case dosing occurs, in a PFR is always an initial dosing. In case no dosing occurs in a non-initial section, the PFR initial conditions are equal to the outlet of the previous reactor section. A PFR is advantageous when the reaction order w.r.t. certain reactant is higher for the reaction which produces the desired product than for other (parallel) reactions and/or reactants. Thus, this reactant needs to have a high concentration level from the beginning.

A PFR is analogous to a standard batch reactor without dosing whereby the feed concentration of the PFR $\boldsymbol{c}_{feed}^{PFR}$ corresponds to the initial concentration of the batch $\boldsymbol{c}_{batch}(t = 0)$. Note, that the residence time τ_f in a PFR corresponds again to the reaction time t_f in a batch reactor.

Continuously Stirred Tank Reactor (CSTR): The CSTR is a limiting case. The time-dependent variables such as $T(t)$ and $\boldsymbol{c}(t)$ reduce to constant values, since a CSTR is ideally mixed in space and assumed to operate in steady-state. One can derive the corresponding balance equations by integration of Eq. (7) over the residence time τ:

$$\int_{\boldsymbol{c}(0)}^{\boldsymbol{c}(\tau)} d\boldsymbol{c} = \int_0^{\tau} \boldsymbol{N}\boldsymbol{r}(T(t), \boldsymbol{c}(t))dt. \tag{8}$$

The steady-states, i.e. the constant state in the reactor which correspond to the outlet states, are defined as $\bar{\boldsymbol{c}}$, whereby $\bar{\boldsymbol{c}} = \boldsymbol{c}(\tau)$, and the constant reactor temperature as $\bar{T}$. Then the integration leads to:

$$\bar{\boldsymbol{c}} - \boldsymbol{c}(0) = \tau \boldsymbol{N}\boldsymbol{r}(\bar{T}, \bar{\boldsymbol{c}}). \tag{9}$$

The resulting balance equation is the standard balance equation for a CSTR:

$$\bar{\boldsymbol{c}} = \boldsymbol{c}(0) + \tau \boldsymbol{N}\boldsymbol{r}(\bar{T}, \bar{\boldsymbol{c}}). \tag{10}$$

This leads to the conclusion that the characteristic dosing policy of a CSTR is either an initial dosing or no dosing. Latter occurs, again, when the outlet stream of the previous reactor is taken directly as inlet of the CSTR. The temperature profile has to be constant. Due to the total back-mixing the product concentrations are higher from the beginning. In the dosing profiles this is realized by product dosing at the beginning of the CSTR section. Due to that, the CSTR is in general preferable when the reactant concentration is supposed to be small or a high (by-)product concentration supports the selectivity w.r.t. the desired product.

Regarding the analogous batch process concept, one can imagine a fed-batch process with constant feed and an initial batch composition corresponding to the outlet concentration of a CSTR $\boldsymbol{c}_{final}^{CSTR}$. This process would have no final reaction time t_f, instead the reaction volume increases in time maintaining the final concentration of the CSTR. Hence, depending on the size of the feed stream the fed-batch would have different steady-state compositions corresponding to certain steady-state concentration of the CSTR.

For a comprehensive description of how to translate these continuous reactor types back into batch reactor types see e.g. [25].

At the beginning of the reaction coordinate an initial dosing takes place to adjust the optimal initial concentrations. Since no reaction can take place without any reactant, this initialization section always appears. From the previously described features of each ideal reactor type one can derive the basic distinction of: distributed (distr.) reactant (R) dosing, initial (init.) reactant dosing, distributed product (P) dosing, initial product dosing and combinations of those. This results into eight possible dosing characteristics. The temperature (T) profile is simply classified in sections of dynamic (dyn.) and constant (const.) behavior. In addition the case of no dosing appears. Therefore the use of the *differential selectivity* is recommended when dealing with selectivity optimization. It allows distinguishing between sections of back-mixing benefit and no back-mixing benefit of the selectivity w.r.t. the desired product, and is calculated at each time point during the dynamic optimization using Eq. 11.

$$\varphi = \frac{moles\ of\ desired\ product\ formed}{moles\ of\ main\ reactant\ consumed} = \frac{\frac{dn_{prod.}}{dt}}{\frac{dn_{react.}}{dt}} \tag{11}$$

In terms of elementary process functions the gradient of the differential selectivity over time is a kind of differential reaction flux, i.e. the change of the ratio of internal fluxes in the reaction network. For the use of the differential selectivity the reactant and the product, which are brought into relation with this measure, have to be specified according to the underlying selectivity problem. The information given by the differential selectivity can also be taken into account in sections of dosing, sometimes simplifying the decision whether back-mixing is really beneficial or not. But, in case of dosing it is not always unambiguous. The mapping of characteristic dosing profiles, temperature profiles and differential selectivity to ideal reactor types and mixing features is shown in Tab. 1. Beside of the classification in Tab. 1 there are a few exceptions or simplifications possible:

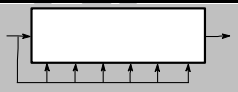
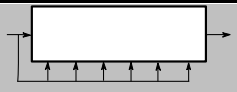
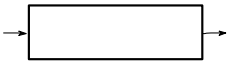
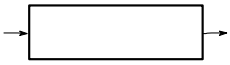
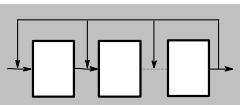
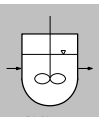
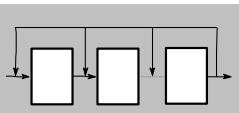
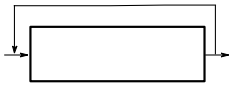
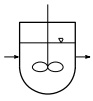
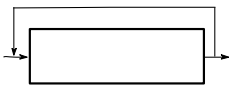
- Despite of a distributed reactant dosing and no product dosing there might be a case where the reactant concentration is hold at a small level (compared to the product concentrations and/or the maximum reactant concentration) by dosing and the product concentration is already high, e.g.

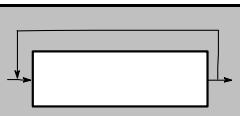
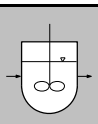
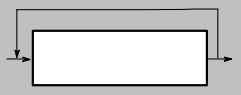
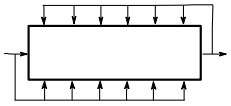
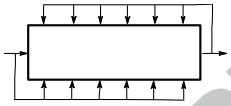
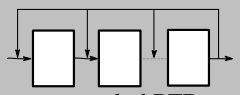
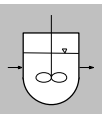
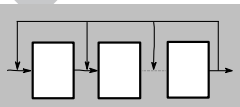
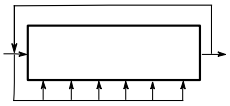
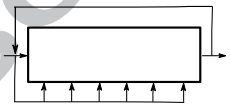
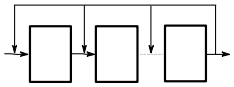
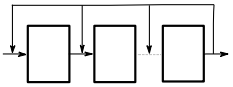
from the previous section. This would indicate a benefit from back-mixing in e.g. a CSTR. In this case it is recommended to take a closer look to the reaction progress, i.e. the concentrations, and the behavior of the differential selectivity.

- All cases of dynamic temperature profiles might in case of very small dynamics be approximated by a constant temperature level.
- A DSR can always be approximated by a cascade of PFR with intermediate reactant dosing or in case of product dosing along the reaction coordinate either by a CSTR cascade or PFR cascade with intermediate dosing. Whether this is beneficial or not strongly depends on the complexity of the distributed dosing profiles.

The sections, which are identified in step 2, can be classified according to Tab. 1 to construct a network of reactors approximating the optimal design from step 1. Thereby, one can analyze neighboring sections to identify possible merging options to reduce the number of network sections, e.g. merge several DSR sections into one DSR or closing a recycle from a subsequent section to the previous, etc. Furthermore, several of the characteristics shown in Tab. 1 can have more than one realization option. By construction of the corresponding reactor-network one has to consider all realizations leading to several reactor-network candidates.

Table 1: Mapping of dosing characteristics and differential selectivity to ideal reactor types.

Dosing	$\frac{dT}{dt} \neq 0$	$\frac{dT}{dt} = 0$
$J_R = distr.$	 DSR	 DSR
$J_R = init.$	 PFR	 PFR
$J_P = distr.$	 PFR cascade	 CSTR or  PFR cascade
$J_P = init.$	 recycled PFR	 CSTR or  recycled PFR

$J_P, J_R = init.$	 recycled PFR	 CSTR or	 recycled PFR
$J_P, J_R = distr.$	 intermediate recycled DSR		 intermediate recycled DSR
$J_P = distr.,$ $J_R = init.$	 recycled PFR	 CSTR or	 PFR cascade
$J_P = init.,$ $J_R = distr.$	 recycled DSR		 recycled DSR
No Dosing			
$\frac{d\varphi}{dt} > 0$	 PFR cascade	 CSTR or	 PFR cascade
$\frac{d\varphi}{dt} < 0$	 PFR		 PFR

3. Results

The proposed approach for reactor-network synthesis is applied to three example processes. Step by step the complexity of the examples increases and the benefits using this method are demonstrated.

A simple set of parallel reactions is used to demonstrate that the numerical solver can identify different reaction sections and chooses the suitable dosing strategy.

The modified van-de-Vusse reaction, which is a well-known literature example for process design, is considered to compare the attainable region determined with the presented approach and the literature results. Moreover, the reactor-network candidates for the optimal point in the AR are derived.

The third example is more complex. It considers again the van-de-Vusse reaction, but without the reversible reaction and under non-isothermal conditions. Here, the connection to superstructure optimization

is shown and it is demonstrated how the *flux profile analysis* can provide a set of superstructure reactor-network candidates.

3.1 Simple Parallel Reactions

In the considered simple reaction scheme A_1 reacts to A_2 and A_3 in parallel:

$$A_1 \xrightarrow{r_1} A_2$$
$$A_1 \xrightarrow{r_2} A_3$$

Scheme 1: Simple parallel reaction

Both reaction rates are described with simple power laws only depending on A_1 but with different reaction orders n and m for reaction rate r_1 and r_2, respectively (Eqs. 12 and 13). Two cases are investigated in which the reaction orders change during the reaction at different time points allowing for a better distinction in the figures:

Case 1: From $n > m$ to $m > n$ at $t = 50\ s$.

Case 2: From $m > n$ to $n > m$ at $t = 52\ s$.

$$r_1 = k_1(T)c_{\mathrm{A}_1}^n \tag{12}$$

$$r_2 = k_2(T)c_{A_1}^m \tag{13}$$

3.1.1 Model Formulation and Optimization Problem

The reaction progress in the batch reactor is described by component mass balances according to Eq. (1). The reactor volume V_R is time-dependent and can be calculated from the total molar holdup and the total concentration of the mixture:

$$V_R = \frac{n_t}{c_t} = \frac{\sum_{\alpha=1}^{N} n_\alpha}{\sum_{\alpha=1}^{N} c_\alpha}, \tag{14}$$

where

$$n_t = n_{A_1}(t) + n_{A_2}(t) + n_{A_3}(t). \tag{15}$$

In combination with the reaction kinetics this leads to the following set of ODEs:

$$\frac{dn_{A_1}}{dt} = V_R\left(-k_1(T)c_{A_1}^n - k_2(T)c_{A_1}^m\right) + j_{A_1}, \tag{16}$$

$$\frac{dn_{A_2}}{dt} = V_R\left(k_1(T)c_{A_1}^n\right) + j_{A_2}, \tag{17}$$

$$\frac{dn_{A_3}}{dt} = V_R\left(k_2(T)c_{A_1}^m\right) + j_{A_3}. \tag{18}$$

The total molar concentration c_t is fixed from the beginning and it is assumed that it does not change significantly. The mass balances of the storage tanks from which the batch reactor is fed are given in Eq. (2). The reactor is considered to work isothermally. Thus, the feed flow rates $\boldsymbol{j}(t)$ are the only time-dependent decision variables in this problem, while $T = T^*$ is a static decision variable.

The optimization aims at maximizing the desired product A_2 within a given time range. At $t = 0$ the batch reactor is empty $\boldsymbol{n}(0) = 0$ and the storage tanks have specified filling levels. To ensure physical correctness the amount of moles are always non-negative $\boldsymbol{n}(t), \boldsymbol{n}_{st}(t) \geq 0$. To allow for an appropriate comparison of the optimization cases some terminal constraints are fixed: (i) the reactant from the storage tank has to be dosed to the reactor up to a maximum value of the remaining storage level ($n_{A_1,St}\left(t_f\right) \leq n_{A_1,st}^{max}$); (ii) the reactant in the reactor has to be consumed up to a given amount ($n_{A_1}\left(t_f\right) \leq n_{A_1}^{max}$); (iii) a minimum amount of product has to be formed ($n_{A_2}\left(t_f\right) \geq n_{A_2}^{min}$). The resulting (DOP) reads:

$$\max_{j_\alpha(t),T,t_f} \left\{n_{A_2}\left(t_f\right)\right\}$$

s.t. Component mass balances:	Eqs. (17) – (19)
Storage mass balances:	Eq. (2)
Dosing constraint:	Eqs. (3)
Reaction rates:	Eqs. (12) – (13)
Constitutive equations:	Eqs. (14) – (15)
Inequality path constraints:	$\boldsymbol{j}(t) \geq 0, \boldsymbol{n}(t) \geq 0, \boldsymbol{n}_{st}(t) \geq 0.$
Terminal constraints:	$n_{A_1,St}\left(t_f\right) \leq n_{A_1,st}^{max} = 0.001,$
	$n_{A_1}\left(t_f\right) \leq n_{A_1}^{max} = 0.01,$
	$n_{A_2}\left(t_f\right) \geq n_{A_2}^{min} = 0.6,$
	$\boldsymbol{n}(0) = 0,$
	$\boldsymbol{n}_{st}(0) = [1, 0.9, 0.1].$
Bounds:	$300\ K\ \leq T \leq 400\ K,$
	$1\ s \leq t_f \leq 100\ s\ .$

The model parameters are given in Tab. 2. The total concentration is set to $c_t = 100 \frac{mol}{L}$.

Table 2: Model parameters of simple parallel reactions example.

$k_{0,1} = 0.5$	$E_{A,1} = 1e4$	$T_{min} = 300$	$\tau_{min} = 1$
$k_{0,2} = 1$	$E_{A,2} = 1.1e4$	$T_{max} = 400$	$\tau_{max} = 100$

3.1.2 EPF Optimization Results

The optimization results for both cases are illustrated in Fig. 6. They indicate that the optimization approach is able to detect the shift in reaction order and reacts appropriately. In case 1 (solid lines) the reactant is dosed completely at the beginning of the process to increase the selectivity to the desired product. In the second reaction zone of case 1 with $m > n$ the content of the storage tanks of the products are fed completely to the batch reactor. This results in lower reactant concentration and thus in smaller formation of the undesired by-product guaranteeing maximum amount of the desired product A_2.

In case 2 (dashed lines) it was necessary to insert an additional constraint, see Eq. (19), to the optimization problem to ensure that reactant is already dosed in the first reaction zone with $m > n$ and that the reaction then starts at $t = 0$,

$$n_\alpha(t) \geq n_\alpha^{min}, \forall \alpha \in \{A_1\}. \tag{19}$$

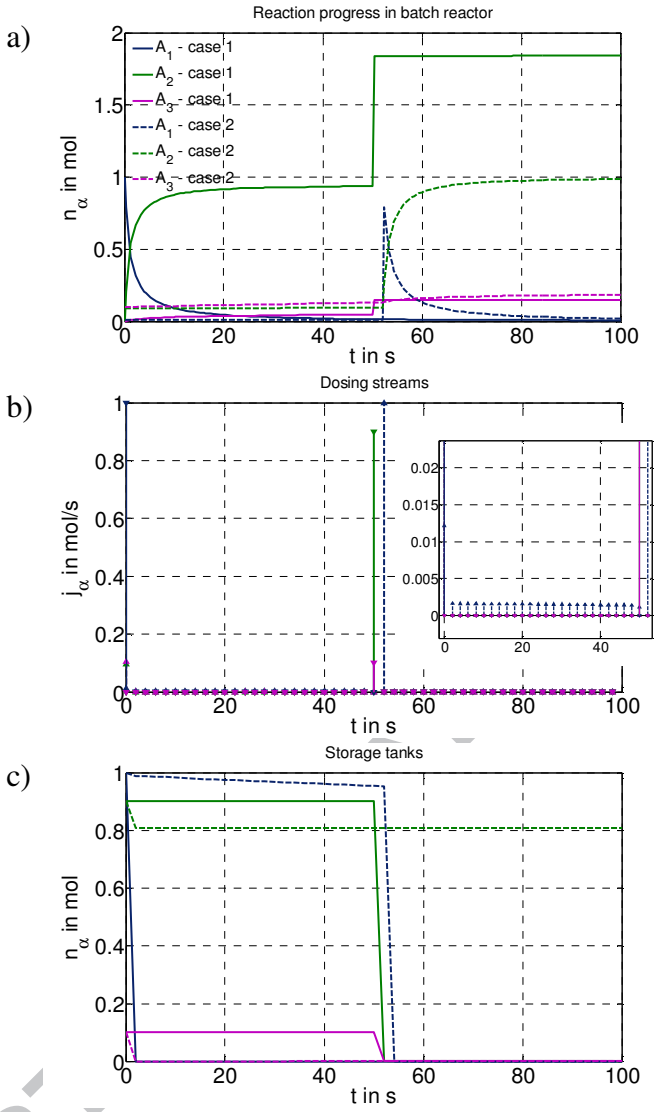


Figure 6: (a) Reaction progress, (b) dosing streams and (c) storage tanks levels for case 1 (solid lines) and case 2 (dashed lines), respectively.

Without this constraint, the solver decides to avoid the first reaction zone with $m > n$ to not waste any reactant. Including this constraint the results shown in Fig. 6 indicate that in the first reaction zone a dosing strategy is chosen on the one hand to maintain a minimum reactant concentration and on the other hand to further decrease the reactant concentration by dosing certain amounts of products. In the second reaction zone the reactant is then again completely fed to the reactor to obtain high reaction rates towards the desired product A_2. Note, that not all products are dosed in the first reaction zone. The benefit of smaller product amounts and thus higher reactant concentration in the second reaction zone is higher than the effect in the first reaction zone. This leads to the conclusion that the dosing strategy is not only qualitatively dependent on

the reaction order. It depends quantitatively on the model parameters and constraint values, e.g. tank levels, as well. In both cases the solver choses an optimal temperature at $T^* = 300\ K$.

3.2 Isothermal, Modified van-de-Vusse Reaction

This example is considered to illustrate how the aforementioned batch scheme can be used to construct the attainable region of a process. There are several approaches given in literature to construct the AR and/or its convex hull (see e.g. [26], [27], [28], [29]).

The classical van-de-Vusse combines a parallel and consecutive reaction in one scheme implying a selectivity problem for the intermediate species. The modified reaction contains an additional reverse reaction from this intermediate species back to the main reactant. The resulting reaction scheme is:

$$A \underset{r_2}{\overset{r_1}{\rightleftharpoons}} B \overset{r_3}{\rightarrow} C$$

$$2A \overset{r_4}{\rightarrow} D$$

Scheme 2: Modified van-de-Vusse reaction

The modified van-de-Vusse process was considered for attainable region analysis already by e.g. Metzger et al. [30] and Burri et al. [31]. Metzger et al. [30] used the classical way of simulating the ideal reactor types from the starting point to first compare the performances and then construct the AR step by step by further simulations from suitable chosen points of the best performing reactor type. This is closely related to the classical AR idea of graphical analysis and construction of the AR which is, however, limited to low-dimensional examples. Burri et al. [31] applied the IDEAS framework using Linear Programming to determine the AR. Both achieved the same attainable region for the given process. For the sake of comparability the same model equations and model parameter as given in the two aforementioned literature sources are used in the following analysis.

3.2.1 Model Formulation and Optimization Problem

In light of the here proposed synthesis approach only the ODEs for the batch reactor are used corresponding to the ODEs for the PFR in the literature sources. The algebraic equations for the CSTR in the literature model are dispensable due to the consideration of a Lagrangian fluid element in the EPF framework. In contrast to the generic formulation in Section 2.2.1, the distributed dosing of components is neglected as it is in the literature example, because in 2-dimensional problems the distributed dosing of

components is not beneficial [13]. Furthermore, the amounts of moles and the reactor volume are combined to concentrations. Simply, because the example gives no option to calculate the volume changes from molar changes. The reaction kinetics is based on simple power laws. The model equations read:

$$\frac{dc_A}{dt} = -k_1 c_A + k_2 c_B - k_4 c_A^2, \tag{20}$$

$$\frac{dc_B}{dt} = k_1 c_A - k_2 c_B - k_3 c_B, \tag{21}$$

$$\frac{dc_C}{dt} = k_3 c_B, \tag{22}$$

$$\frac{dc_D}{dt} = k_4 c_A^2, \tag{23}$$

with $k_i, \forall i \in \{reactions\}$ as reaction coefficients and $\boldsymbol{c}$ are the concentrations of all components. Parameters and initial conditions are adopted from the aforementioned literature sources with $k_1 = 0.01\ s^{-1}$, $k_2 = 5\ s^{-1}$, $k_3 = 10\ s^{-1}$, $k_4 = 0.01\ m^3 kmol^{-1} s^{-1}$ and $c_A^0 = 1$, $c_B^0 = c_C^0 = c_D^0 = 0$, respectively [30].

The optimization problem is stated as follows:

$$\max_{t_f} \ c_B(t_f)$$

s.t. Component mass balances: Eqs. (21) – (24)

Inequality path constraints: $\boldsymbol{c}(t) \geq 0,$

Initial conditions: $\boldsymbol{c}(0) = [1, 0, 0, 0].$

3.2.2 EPF Optimization Results

At first, the FPA approach is used to find an optimal reactor-network maximizing the final concentration of B. Since the temperature and the mass dosing are not part of the optimization, the focus lies on the analysis of the differential reaction flux. The result of the dynamic optimization stated before is depicted in Fig. 7.

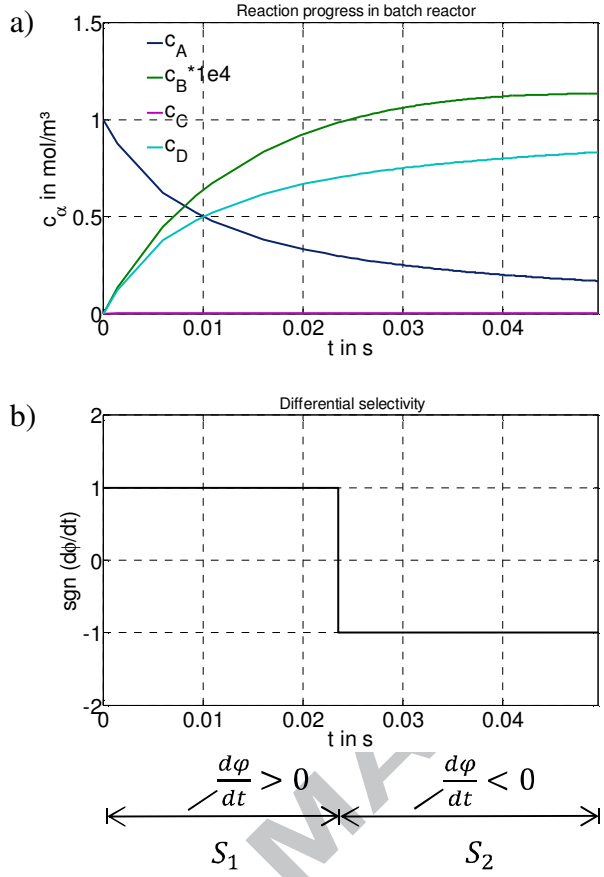


Figure 7: (a) Reaction progress; (b) Differential reaction flux.

The differential reaction flux is positive in the first and negative in the second reaction section indicating a back-mixing benefit in the first and no benefit from back-mixing in the second section. As there is no dosing and temperature control, the association with reactor types is obvious leading to reactor-network of a CSTR for the first reaction section and a PFR for the second. The optimal concentration of B achieved in the optimization is $c_B^{max} = 1.13 * 10^{-4} kmol/m^3$. Note, that this is the optimum using only a PFR, which corresponds to the Lagrangian description used for the optimization. The benefit of the use of a CSTR in the first reaction section takes effect when optimizing the derived optimal reactor-network consisting of CSTR and PFR. This leads to an optimum at $c_B^{max} = 1.24 * 10^{-4} kmol/m^3$, which is in accordance to literature [30, 31].

In a second step, the same approach is used to construct the attainable region of the process. For this purpose, the differential reaction flux is included in the dynamic optimization to switch between the balance equation for the PFR and the CSTR, see Eq. (24). This is possible since a simultaneous optimization framework is used (see Section 4.1).

$$\boldsymbol{c}(t_i) = \begin{cases} \boldsymbol{c}(t_{i-1}) + \frac{d\boldsymbol{c}}{dt_i}\,, & if\ \frac{d\varphi}{dt_i} < 0 \\ \boldsymbol{c}(t_{i-1}) + \tau \boldsymbol{Nr}(\boldsymbol{c}(t_i)), & if\ \frac{d\varphi}{dt_i} > 0 \end{cases} \qquad \forall i \in \{discretized\ elements\} \tag{24}$$

The AR of this example is constructed in the $[c_A, c_B]$-space, such as introduced in literature [30, 31]. To use the presented dynamic optimization framework for AR construction, the optimization aiming at maximum c_B is carried out for different specified final values c_A^f.

The resulting dynamic optimization problem reads:

$$\max_{t_f} c_B(t_f)$$

s.t. Component mass balances: Eqs. (21) – (24)

Inequality path constraints: $\boldsymbol{c}(t) \geq 0$,

Initial conditions: $\boldsymbol{c}(0) = [1, 0, 0, 0]$,

Switching condition: Eq. (24),

Terminal constraint: $c_A(t_f) = c_A^f$.

The results of several runs of this optimization for scanning c_A^f from 0 to 1 are shown in Fig. 8 (purple, dashed line). The dynamic optimization based results indicate as shown before the use of a CSTR and a subsequent PFR as optimal reactor-network to reach all points of the shown AR. But the hull of the AR is not convex in the range of $0.4 \leq c_A \leq 1$. In the classical AR approach those concave regions can be closed by mixing of streams from different points of the AR. In our approach it can be identified by optimal dosing of components, e.g. inlet stream along the reaction coordinate. Since this was neglected (see above), the concept of dosing has to be reduced to by-passing only to find at least benefits from mixing reactor inlet and outlet streams. This is realized by changing the definition of the final values of the concentrations in the dynamic optimization problem above. The objective function is changed to:

$$\max_{t_f, \varepsilon} c_B^f = \varepsilon * c_B(t_f) + (1 - \varepsilon) * c_B(0), \tag{25}$$

and the terminal constraint for definition of the final value of A is replaced by:

$$c_A^f = \varepsilon * c_A(t_f) + (1 - \varepsilon) * c_A(0), \tag{26}$$

whereby $\varepsilon\ \epsilon\ [0,1]$ is a mixing factor deciding about the mixing fractions of inlet and outlet stream.

The calculation of the AR, considering these modifications, with the same procedure as stated before leads to the blue, solid line in Fig. 8 which matches exactly the results from literature [30, 31]. The inclusion of the by-pass modification is not generic. In case of a by-pass within the reactor-network this would not work

anymore. Then one can proceed in the same way as done in the classical AR approach and simply reach the points of the convex hull by mixing of available streams.

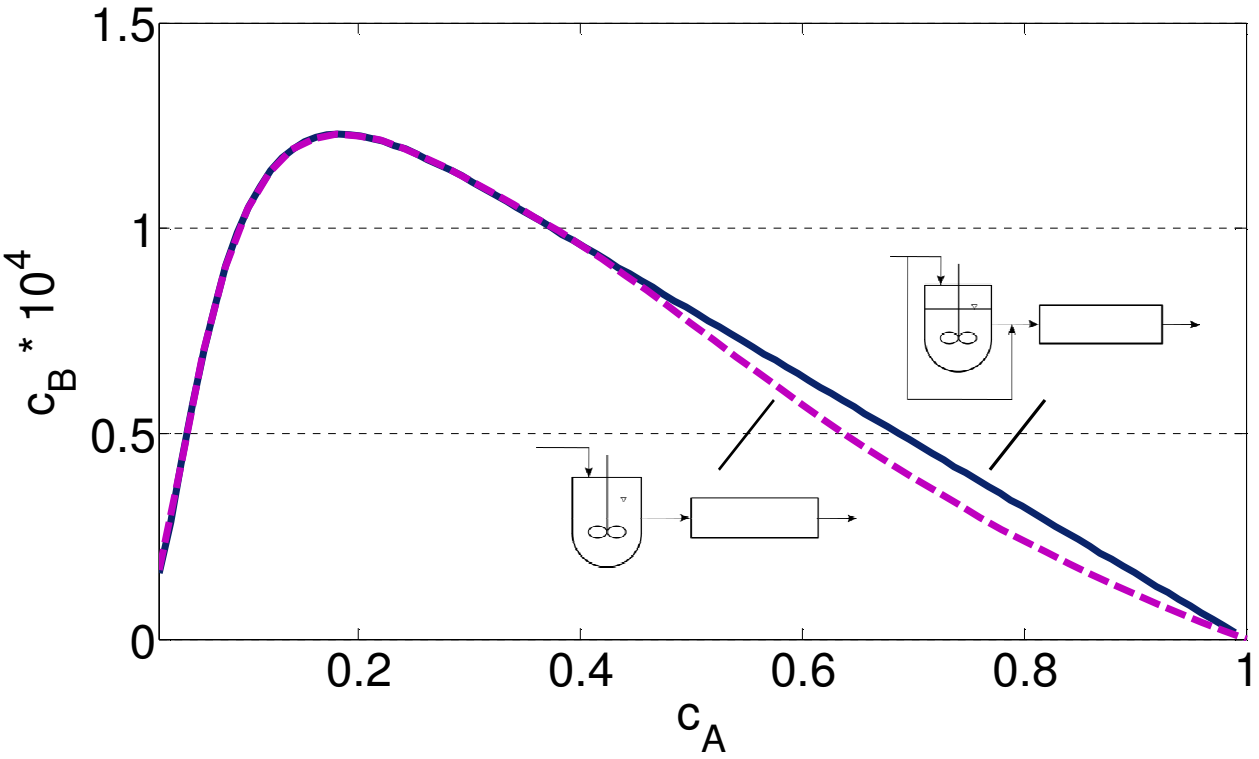


Figure 8: Attainable region constructed by the presented dynamic optimization based approach without by-pass mixing (purple, dashed line) and with by-pass mixing (blue, solid line).

3.3 Non-isothermal, Standard van-de-Vusse Reaction

In the following it is demonstrated on the non-isothermal, standard van-de-Vusse reaction, how the presented synthesis approach can be used as well for non-isothermal reactions and which additional degree of freedom in the flux analysis thereby arises. To show as well, how the method can be used to find suitable candidates for a subsequent optimization of process structures, the van-de-Vusse reaction is an example of good comparability, since already superstructure optimizations were carried out in several research works in the last decades (see. e.g. [18] and [21]). The reaction scheme reads:

$$A \xrightarrow{r_1} B \xrightarrow{r_2} C$$
$$2A \xrightarrow{r_3} D$$

Scheme 3: Non-isothermal, standard van-de-Vusse reaction

3.3.1 Model Formulation and Optimization Problem

The standard van-de-Vusse reaction scheme has only three reactions since the reaction from A to B is irreversible. For incorporating a temperature dependency to the reaction rates the standard Arrhenius law is used:

$$k_i = k_{0,i}\, exp\left(\frac{-E_{A,i}}{RT}\right), \forall i \in \{reactions\}, \tag{27}$$

where E_A are the activation energies, R is the universal gas constant and T is the temperature. To allow for concentration changes by dilution, the volume has to be considered in particular. Thus, the model equations in terms of moles read:

$$\frac{dn_A}{dt} = V_R(-k_1 c_A - k_3 c_A^2) + j_A, \tag{28}$$

$$\frac{dn_B}{dt} = V_R(k_1 c_A - k_2 c_B) + j_B, \tag{29}$$

$$\frac{dn_C}{dt} = V_R(k_2 c_B) + j_C, \tag{30}$$

$$\frac{dn_D}{dt} = V_R(k_3 c_A^2) + j_D, \tag{31}$$

and the resulting volume of the reaction mixture is calculated via Eq. (14), whereby the total concentration is fixed to the same value which is used in literature as initial concentration, $c_t = 1\, mol/L$. The parameters for the kinetic coefficients in Eq. (27) are given in Tab. 3; the initial conditions for the optimization are the same as previously shown in Section 3.2.

The resulting optimization problem is formulated as:

$$\max_{\boldsymbol{j}(t), t_f, T(t)} \left\{ n_B(t_f) - \left(n_{B,st}(0) - n_{B,st}(t_f) \right) \right\}$$

s.t. Component mass balances: Eqs. (28) – (31)

Storage mass balances: Eq. (2)

Dosing constraint: Eqs. (3)

Constitutive equations: Eqs. (14) – (15)

Inequality path constraints: $\boldsymbol{j}(t) \geq 0, \boldsymbol{n}(t) \geq 0, \boldsymbol{n}_{st}(t) \geq 0,$

Initial conditions: $\boldsymbol{n}(0) = 0,$

$\boldsymbol{n}_{st}(0) = [1,2,2,2].$

The initial storage tank levels of the products are set to a higher value than the reactant level to better highlight the effect of possible product dosing.

Table 3: Model parameters of non-isothermal, standard van-de-Vusse reaction.

$k_{0,1}$	$k_{0,2}$	$k_{0,3}$
$1.5 \times 10^6 s^{-1}$	$4.4 \times 10^8 s^{-1}$	$100\ L\ mol^{-1} s^{-1}$

$E_{A,1}$	$E_{A,2}$	$E_{A,3}$
$6.6274 \times 10^4 J\ mol^{-1}$	$9.9411 \times 10^5 J\ mol^{-1}$	$3.3137 \times 10^4 J\ mol^{-1}$

3.3.2 EPF Optimization Results

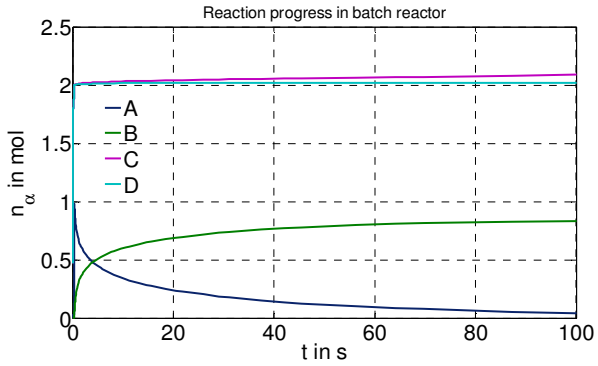
The results of the EPF optimization of the non-isothermal, standard van-de-Vusse reaction are shown in Fig. 9. The maximum objective is reached with $Obj = 0.8318$. This value is in the same range as documented in literature. Note, that most of the articles give the optimal concentrations of B as measure of their process designs. But, the objective given here can be compared directly to these values since the total concentration is $c_t = 1\ mol/m^3$ and the overall amount of component A added to the process is $n_A^t = 1\ mol$. The optimal dosing fluxes indicate that it is beneficial to dose reactant and by-products at the very beginning of the process. Note, that the reason for the by-product dosing is not the dilution of the reactant, instead the product B is supposed to be diluted. This is owed to the very high reaction rates already at the beginning due to the chosen temperature control.

The solver chooses a trade-off between (i) high temperature at the beginning, which supports r_1 and r_3 more due to the high activation energy of r_2, and (ii) the best ratio of concentrations of components A and B. To inhibit the parallel reaction from A to D, reactant A is completely dosed at the beginning. But to inhibit the consecutive reaction r_2 as well, the concentration of B should be low and therefore the dilution via by-product dosing is preferred.

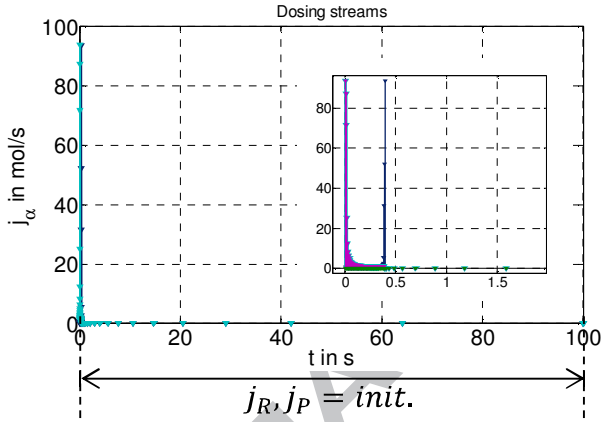
Dividing the dosing and temperature control profiles into characteristic sections, such as shown in Section 2.1, one ends up with (i) a first reaction section S_1 with initial dosing of reactant and by-products, a dynamic temperature dosing and negative gradient of the differential selectivity; (ii) a second reaction section S_2 without dosing but still a dynamic temperature control and a positive gradient of the differential selectivity; and (iii) a third longer reaction section S_3 without dosing, an almost constant temperature control and again a positive gradient of the differential selectivity. The boundary between S_2 and S_3 is not fixed and at the end a

question of the subsequent detailed process design. The look-up table (Tab. 1) suggests for an initial dosing of reactant and products with dynamic temperature control and a negative gradient of the differential selectivity like in S_1 a PFR with recycle. The reaction section S_2 has no dosing, a dynamic temperature control and a positive gradient of the differential selectivity. This could be realized in a cascade of PFRs with intermediate recycles. S_3 shows a similar characteristic whereby the temperature control can rather be approximated as constant. Thus, it can be realized with a CSTR. Depending on the positioning of the boundary of the second and third reaction section or even their merger, it appears reasonable to realize both sections in either one CSTR assuming a constant temperature approximation, or a cascade of PFRs with intermediate recycles, which allows for dynamic temperature control. The resulting reactor-network candidates are depicted in Fig. 10.

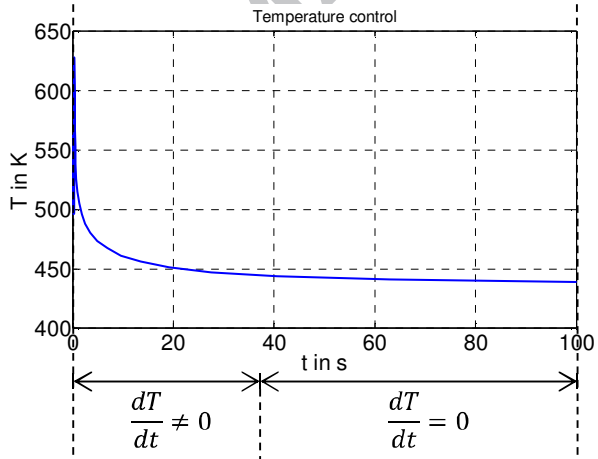
a)



b)



c)



d)

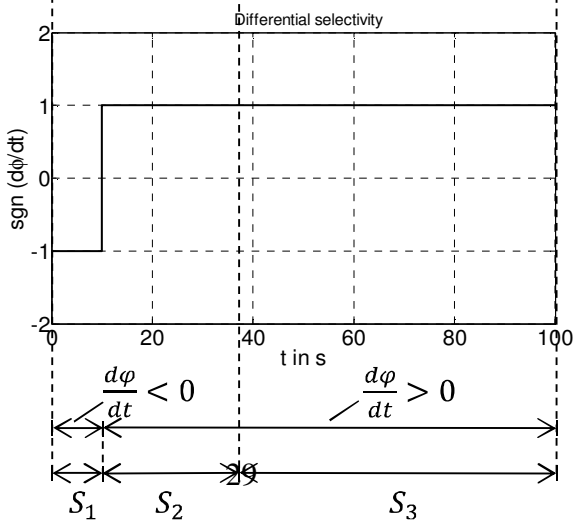


Figure 9: (a) Reaction progress; (b) Dosing streams; (c) Temperature control; (d) Differential reaction flux.

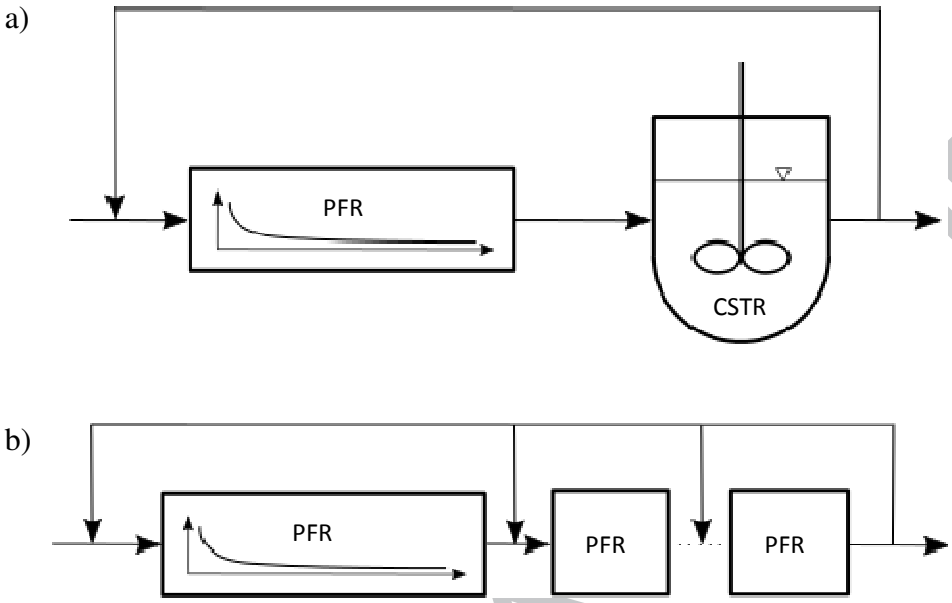


Figure 10: Candidates for optimal reactor-networks for non-isothermal, standard van-de-Vusse reaction: (a) PFR with distributed temperature control and CSTR for internal back-mixing; (b) PFR with distributed temperature control and cascade of PFRs with intermediate recycles.

The results indicate benefits from internal recycling (back-mixing) in the second reaction section and global recycling to the inlet of the reactor-network. A third important aspect is the realization of the sharp temperature profile in the first reaction section. The proposed reactor-networks in Fig. 10 are candidates including all of these aspects. For a detailed quantitative analysis these two reactor-network candidates should be augmented by simpler reactor-networks neglecting e.g. the global recycle or approximate the sharp temperature control by a simpler profile. In this way the impact of these aspects on the real performance of the reactor-networks can be identified and a better decision-making is possible, e.g. when it comes to an economic evaluation.

Neglecting for instance the global recycling of byproducts, the candidate given in Fig. 10 (a) is in good accordance to the superstructure optimization results of Schweiger and Floudas [21] who proposed a network of a PFR with optimal temperature control and a subsequent CSTR. Note, that this CSTR has a much higher residence time than the PFR and, thus, the back-mixing takes place almost over the entire reaction time, which might indicate also a benefit of a global recycling. Kokossis and Floudas [18] optimized a network of CSTRs with intermediate cooling, indicating a similar temperature characteristic as shown in Fig. 9 (c). Their

results indicate as well a first section where no recycling takes place and a second section where recycling takes place. But this recycling is stated to act as cooling medium, and a global recycle is not included.

4. Discussion

4.1 Numerical Solution Approach

The dynamic optimization of the batch scheme illustrated in Fig. 4 is the backbone of the proposed approach. The solution of this dynamic optimization problem is achieved by direct transcription of the dynamic optimization problem with orthogonal collocation on finite elements, see e.g. [32]. For solving the resulting nonlinear programming problem the solver CONOPT V3.14 is used in AMPL (A Mathematical Programming Language). Pre-investigations were carried out comparing this method with a single shooting approach and Pontryagin's Maximum Principle [33] regarding feasibility, convergence speed and interpretability of the optimization results for the simple example in section 3.1. The orthogonal collocation on finite elements was superior to Pontryagin's Maximum Principle due to its direct solution. The dependency on the initial values was much less and no complex adjustment of tuning parameters was necessary. Nevertheless, indirect methods such as Pontryagin's Maximum Principle are a promising tool for dynamic optimization of batch processes, in which mixed and pure path constraints are active throughout operation as shown in [34].

In comparison to the single shooting approach the simultaneous solution is advantageous, because the dosing at each finite element can be handled more easily.

4.2 Relation to Attainable Region Approach

In light of a comparison of the EPF methodology for process design with the attainable region approach, the second example in section 3.2 revealed that the main difference and possible advantage of a dynamic optimization approach is the direct determining of an optimal process design. While the AR approach determines the whole region of attainable states, i.e. concentrations, the FPA seeks for a particular optimal design consisting of the optimal reactor-network and its control by heat and mass fluxes. This allows on the one hand for a direct adaptation of the results for an optimal control strategy for a batch process and on the other hand for a direct translation into candidates for optimal continuous reactor networks. Since the FPA is not tailored to construct the AR of a process, several adaptations have to be made to use it for this purpose, e.g. the transformation from mass/moles to concentrations. The construction of an attainable region for the

proposed batch scheme is then simply possible by solving a series of dynamic optimizations to determine the convex hull of the corresponding AR.

The example shown in Section 3.2 does not include the distributed dosing of components. This is of interest for higher dimensional problems ($n \geq 3$). Feinberg [35] and Hillestad [23] demonstrated how the distributed dosing in a DSR can be introduced to the construction of an AR and a corresponding dynamic optimization problem, respectively.

4.3 Relation to Superstructure Optimization

The superstructure optimization is often used for process design purposes, especially for reactor-network synthesis. With nowadays computational power even very large-scale NLPs and MINLPs can be solved to find the optimal process configuration. Both, the isothermal and the non-isothermal process example in sections 3.2 and 3.3, respectively, resulted in possible candidates for process structures, which can be used for further superstructure optimizations. The proposed FPA approach is, thus, a tool for the rational selection of candidate superstructures for a subsequent more detailed optimization of those. As already Achenie and Biegler [16] stated in one of the fundamental articles about superstructure optimization, one of the main challenges is to figure out suitable candidates. A special feature of the synthesis of candidates with the proposed *flux profile analysis* approach is that it bases on reaction engineering fundamentals.

A detailed process design based on the pre-selected reactor-networks with a superstructure optimization approach would result in exact values concerning residence times and the corresponding reactor volumes, the feed and recycle stream compositions, and as well the sizing of possible auxiliary units such as heat exchangers or separators. This detailed process design is indispensable to compare different reactor-network candidates, their benefits in an overall process and resulting costs. The pre-selection only provides qualitative information.

Note, that the presented synthesis procedure can provide quantitative information for the subsequent detailed process design. For instance, the initialization phase of the dosing policy indicates in which bounds the concentrations of different components in the recycle streams might be. In general, the values of states and controls of the dynamic optimization point out suitable bounds on states and controls of the detailed process design. This restricts the search space for optimization on a rational basis leading to reduced computational effort.

4.4 Hints on Translation from Batch Process to Continuous Reactor-Network

As introduced in this work, the main information about how to associate dosing policies with ideal reactor types lies in the analysis of the dosing fluxes, and in case of non-isothermal processes as well the temperature profiles. But it is, nevertheless, highly recommended to use the information of the reaction progress in the batch reactor as well, especially in cases which are ambiguous. Then, one can, for instance, also just include an integer decision in the further detailed process design or just generate several reactor-network candidates including different options for the ambiguous reaction section, as proposed in Section 3.3.2.

The decision, whether it is beneficial to realize product dosing by simple back-mixing or by dosing of pure species, e.g. from a separation subsequent to the reaction, is a question of e.g. separation quality, costs of back-mixed reactor systems and the prices of the pure species and, thus, of detailed process design. The same holds for the realization of possible beneficial back-mixing either in a CSTR system or with a cascade of PFRs with intermediate recycles.

4.5 Hybrid Batch-Continuous Reactor-Networks

A further advantage of the presented design procedure is the possibility to synthesize networks of batch and continuous reactors. Since the batch control is calculated already in the dynamic optimization, particular reaction sections might be realized discontinuously, i.e. in repeated batch mode, instead of translating them to continuous reactor types. For certain conditions, i.e. dynamic temperature control and distributed dosing policies, this is of advantage, since the realization in a continuous reactor might be in this case more complex and expensive. Furthermore, reaction sections which are realized in a repeated batch reactor are more flexible, because an adaption to new production demands can be realized by only changing the computer process control instead of changing the entire reactor equipment.

5. Conclusion

This work introduces a new concept for synthesis and rational selection of optimal reactor-network candidates based on the methodology of elementary process functions (EPF) [1]. Core of the approach is the dynamic optimization of a special batch configuration which leads to optimal dosing profiles of reactants and products, and heating/ cooling strategies. The resulting optimal control profiles are subdivided in characteristic reaction sections which are analyzed to identify suitable continuous reactor types for each section and, hence, construct reactor-networks.

Although this synthesis approach allows for determining the attainable region of a process, the main advantage is the direct determination of an optimal reactor-network or possible candidates for given

specifications. For higher dimensional problems, than investigated here, the computational effort for constructing the AR with the presented dynamic optimization based approach might be larger in comparison to state-of-the-art approaches which are tailored for this purpose. Nevertheless, it was shown successfully that the optimal reactor-network found with the *flux profile analysis* matches to the literature results.

The analysis of the continuous reactor-network candidates determined with this approach gives new insights when compared to the results achieved by superstructure optimization in literature. This indicates that the reactor-network candidates determined by the *flux profile analysis* can be used as a reliable basis for subsequent superstructure optimization. Thereby, the complexity of the superstructure to be investigated can be reduced significantly, and the quantitative results of the DOP can serve as bounds or initial guesses for states and controls of the units and fluxes in the superstructure optimization.

This work closes gaps between these state-of-the-art methods for continuous reactor-network synthesis and dynamic optimization based reactor design or rather reactor-network synthesis methods. Furthermore, it allows for applying dynamic optimization based methods, which are mostly used for batch optimization or in combination with predefined superstructures, for continuous reactor-network synthesis and simplifies the synthesis of hybrid networks of continuous and discontinuous reactor units.

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This work is part of the Collaborative Research Centre “Integrated Chemical Processes in Liquid Multiphase Systems” - InPROMPT. Financial support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged (TRR 63).

Nomenclature

Latin symbols

A, B, C, D	chemical components	-
c	concentration	mol/m^3
e	basic vector	-
E_A	activation energy	J/mol
g	control fluxes	-
j	molar flux	mol/s
k	chemical reaction coefficient	$various$
m	reaction order	-
n	amount of moles, reaction order	mol
N	stoichiometric matrix	-

N_R	number of reactants	-
N_P	number of products	-
r	reaction rate	mol/s
R	universal gas constant	$J/mol/K$
S	section	-
t	time	s
T	temperature	K
V	volume	m^3
x	arbitrary state	-
X	conversion	-

Greek symbols

ν	stoichiometric coefficient	-
φ	differential selectivity	-

Abbreviations

AR	attainable region
CSTR	continuous stirred tank reactor
DOP	dynamic optimization problem
DSR	distributed/differential sidestream reactor
EPF	elementary process functions
MINLP	mixed integer nonlinear programming
NLP	nonlinear programming
Obj	objective
PFR	plug flow reactor

Subscripts & Superscripts

α	chemical components
f	final
k	direction in state space
m,n	reaction order
max	maximal
min	minimal
P	product
R	reactant
set	predefined
st	storage

t	total
0	initial

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Highlights include

- structured reactor-network synthesis framework based on dynamic optimization
- operational mode independent synthesis approach including hybrid continuous/discontinuous realizations
- identification of benefits from back-mixing and recycles within the network
- synthesis of reactor-network candidate for super structure based process design
- construction of the attainable region via dynamic optimization