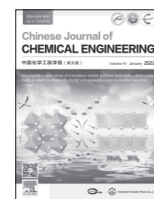




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Review

Recent progress on equation-oriented optimization of complex chemical processes

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ABSTRACT

Process optimization in equation-oriented (EO) modeling environments favors the gradient-based optimization algorithms by their abilities to provide accurate Jacobian matrices via automatic or symbolic differentiation. However, computational inefficiencies including that in initial-point-finding for Newton type methods have significantly limited its application. Recently, progress has been made in using a pseudo-transient (PT) modeling method to address these difficulties, providing a fresh way forward in EO-based optimization. Nevertheless, research in this area remains open, and challenges need to be addressed. Therefore, understanding the state-of-the-art research on the PT method, its principle, and the strategies in composing effective methodologies using the PT modeling method is necessary for further developing EO-based methods for process optimization. For this purpose, the basic concepts for the PT modeling and the optimization framework based on the PT model are reviewed in this paper. Several typical applications, e.g., complex distillation processes, cryogenic processes, and optimizations under uncertainty, are presented as well. Finally, we identify several main challenges and give prospects for the development of the PT based optimization methods.

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1. Introduction

Modern chemical and petrochemical industries are tending to be upgraded by coupling, integrating, and recombining traditional elementary processes to configure new processes. And the objective is to reduce energy consumption and environmental impact significantly, and, at the same time, achieve better economic performance and abilities to accommodate changing feedstocks and energy sources. Supporting such reconfigurations requires extensive mathematical modeling, simulation, and optimization to ensure the expected advantages of the processes [1–3]. One of the major achievements in Process Systems Engineering as a discipline is the success in chemical process simulation, and this leads to the appearance of several powerful tools that have been widely adopted for process simulations, e.g., Aspen PlusTM and others, for both practical application and research purposes.

Simulation of steady-state chemical processes is based on solving nonlinear algebraic equation systems by Newton type

methods. Given the availability of effective tools for process simulations, integrating the solutions of algebraic equation systems into an optimization framework has been one of the main attempts in developing methodologies of chemical process optimization. In this attempt, approaches fall roughly into two categories. Gradient-based optimization approaches are usually preferred as they need much fewer function evaluations by process simulations and can mathematically guarantee a rigorous and global optimum [4,5]. Non-gradient-based approaches usually employ random searches [6–9] or learning methods using data sets derived by solving the process models or surrogate models by regression [10,11]. The non-gradient-based approaches have been shown robust in some cases but computationally expensive and unable to guarantee global optimal solutions [12,13].

The gradient-based optimization approaches have inherent advantages in making use of the gradient information from the process simulation. However, mathematical model equations describing the steady-state operations in chemical processes comprise large-scale systems of nonlinear algebraic equations, and solving these systems is challenging for practically-relevant problems. The equation systems are large-scale because recycle structures of the process flowsheets make model equations describing the unit operations in the cycles highly coupled. Despite significant

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progress in handling large-scale matrices, finding an initial point to converge Newton type methods remains challenging.

Two main strategies have been used to handle such a large-scale equation system: the modular-oriented approach (MO, also termed as sequential modular, SM) and the equation-oriented strategy (EO). The SM approach, which is more widely applied and usually a default approach in almost all the main commercial simulators, is based on “tearing” recycle streams and solving the units in the cycles sequentially in an iteration loop for the teared streams convergence. The SM approach can significantly mitigate the initial point issue by reducing the number of coupled equations to unit scale. In the optimization service, however, gradient matrices need to be evaluated by inaccurate but computationally expensive numerical differentiation (finite difference) calculations, frequently causing optimization failures in the SM environments [14–17]. On the contrary, the EO method solves all the equations in the flowsheet simultaneously. Especially, the EO approach is more advantageous than the SM approach for process optimization. This is because accurate and cheap automatic differentiation for estimating gradient matrices is accessible in the EO environments of main simulation packages [14–17]. However, when rigorous unit operation models are adopted in the EO environments, the simulation of the complex flowsheet is usually very difficult, making optimization even more intractable. This is because, when all the nonlinear equations in a flowsheet are solved simultaneously, the Newton type method requires a good initial point that must be close enough to the actual solution of the system equations, which is extremely difficult to achieve [18–20]. As a consequence, solving the entire flowsheet model is rarely pursued in practice, and current computational approaches predominantly rely on user-informed decompositions to reach a solution [21,22].

From the above perspective, the EO-based method can be potentially effective for rigorous optimization of chemical processes only if the initial point issue can be effectively addressed.

Recently, breakthroughs in this aspect have been made by relaxing some of the model equations into differential equations, which are statically equivalent to the original algebraic equations. By using this scheme, also termed as pseudo-transient (PT) model assisted method, if an initial point fails to converge the Newton method, it is used as an initial condition to start the pseudo-time integration of the differential–algebraic equation (DAE) system until the system reaches a point within the Newton convergence basin [23]. Series of investigations in this line have been reported in the literature and shown that the EO-based optimization is forming a new platform for large-scale and complex chemical process optimization.

In this paper, we briefly review the recent development on the EO-based optimization approaches, emphasizing the PT assisted methods, their advances, applications, and the challenges in perspective, hoping to provide a guideline for future research.

This paper is organized as follows. In Section 2, we introduce the pseudo-transient modeling method and its corresponding optimization algorithm framework. In Section 3, we present the application of the PT model. In Section 4, we discuss the current challenges and prospects of the PT modeling. Finally, we highlight the main points of this review in Section 5.

2. Pseudo-Transient Modeling and Optimization Algorithm Framework

Pattison and Baldea [23] proposed a pseudo-transient continuation (PTC) method to address the convergence problem for Newton type methods in EO environments for complex chemical process optimization. The PTC as a numerical method has been shown to effectively extend the convergence basin of algebraic

equations [24]. This is achieved by converting the algebraic equations (AEs) into differential–algebraic equations (DAEs), and thus the initial value problem in the Newton-type solvers is replaced by the initial condition problem in the solving of the DAE system.

With the improved convergence abilities, the PT modeling has found applications in the simulation and optimization of large-scale flowsheets [25–29]. These applications are crucial to modern chemical processes, which often rely on new, complex equipment for improved economic and energy efficiency.

Due to the efficient and advanced characteristics of the pseudo-transient modeling as well as its wide applications in the optimization of complex process systems, the following subsections are dedicated to describing the state-of-the-art pseudo-transient (PT) modeling method, which includes the basic concepts of PTC, the pseudo-transient flowsheet modeling and simulation, and the optimization framework based on PT models.

2.1. Pseudo-transient continuation (PTC) method

PTC method is a globalization technology for computing the steady-state solution of complex problems described by ill-conditioned models [24,30] by conducting pseudo-time integration from initial conditions. The essence of the method consists of converting a system of AEs to DAEs by incorporating the natural dynamics of the process, and thus the initial value problem in Newton-type solvers can be replaced by the initial condition problem in the solving of the DAE system. Assuming the original problem exists stable solutions, the PTC method would converge to stable solutions more robustly than the conventional Newton's method in solving nonlinear equation systems.

In general, the integral computation for dynamic equations is relatively stable for a real-world dynamic process if the problem is not ill-conditioned. However, it would take a long time for such integral computation to approach a steady-state solution for the process. In addition, real dynamic rigorous models, such as the rigorous dynamic model of the distillation process, need complex hydraulics correlations to make the DAE system squared before the system simulation. The hydraulics correlations, which are not readily available at the design stage, may lead to a higher index of the DAEs of the systems [31]. Consequently, it is inconvenient to use the actual dynamic process model to solve the convergence problem of the steady-state simulation. In the PT assisted approach, however, it is not necessary to integrate a real dynamic process model, because only the result at the end of the time integration is required to be identical with the steady state solution of the original algebraic equations, and the path of the integration does not matter. So, a well-posed virtual transient process can be composed based on static equivalent principle, guaranteeing a result of the same steady state. In fact, in addition to the PTC method, the homotopy continuation (HC) method [32–34], has been used for a long time to solve algebraic equations. Compared with HC, a PTC method has a significant advantage of preserving the physical meaning of models during the continuation evolution and, as a result, can exhibit more stable conversions.

2.2. Pseudo-transient modeling

Based on the insights from the PTC method, simple transient process models, which are statically equivalent [35] to the steady-state ones, should be provided. Pattison and Baldea [23] provided general guidance for constructing pseudo-transient models of unit operations. The major step was to convert a part of the original algebraic model equations into differential equations. As such, the system of AEs for the steady-state processes is converted to a system of DAEs, which can be solved by time integral from an initial condition until a steady-state is achieved, when a Newton

method for solving the AEs fails to converge. The algebraic equations chosen for conversion are usually those with strong nonlinearity or coupling effect with others.

The idea of a PT model is to assume that the derivative of a state variable is proportional to the residual of the static balance equation. The general structure of the expression of differential equations can be given as:

$$\tau_x \frac{dx}{dt} = \text{CONV} + \text{GEN} + \text{FLUX} \quad (1)$$

where x is a state variable; t is the pseudo-time; τ_x is a time constant that influences the integration performance; CONV represents the convective terms in the unit (i.e., inlet and outlet material and energy flow rates); GEN represents the rate of generation (or consumption, e.g., the material and heat generation/consumption caused by chemical reactions); and FLUX represents the non-convective addition or subtraction of material or energy (e.g., the heat exchanged with the environment).

The terms GEN and FLUX in Eq. (1) would contribute to nonlinearity and stiffness of the process models and increase the difficulty of the solution procedure. To deal with this problem, a continuation parameter α is introduced to modulate these nonlinear terms. The parameter α can be known as a state variable which is initially zero, but increases gradually to 1 at a steady state. The corresponding equations are given by:

$$\begin{aligned} \tau_p \frac{d\alpha}{dt} &= 1 - \alpha \\ \alpha(t=0) &= 0 \end{aligned} \quad (2)$$

where τ_p is a time constant.

For the purpose of illustration, we take the PT modeling procedure of a reactive distillation (RD) column as an example [36]. The traditional MESH (mass balance, phase equilibrium, summation and heat balance) equations describing a reactive distillation stage are given as follows.

Material balance (M):

$$0 = V^{j+1}y_i^{j+1} + L^{j-1}x_i^{j-1} - V^jy_i^j - L^jx_i^j + R_i^jV_r^j \quad (3)$$

$$i = 1, 2, \dots, Nc; \quad j = 1, 2, \dots, Ns$$

Phase equilibrium (E):

$$y_i^j = k_i^j x_i^j \quad (4)$$

$$i = 1, 2, \dots, Nc; \quad j = 1, 2, \dots, Ns$$

Summation (S):

$$\sum_{i=1}^{Nc} x_i^j = 1, \sum_{i=1}^{Nc} y_i^j = 1 \quad (5)$$

$$j = 1, 2, \dots, Ns$$

Heat balance (H):

$$0 = V^{j+1}h_v^{j+1} + L^{j-1}h_l^{j-1} - V^jh_v^j - L^jh_l^j \quad (6)$$

$$j = 1, 2, \dots, Ns$$

where index i and j refer to the component and the stage number, respectively; L and V are the liquid and vapor flow rates leaving each stage; x and y are the liquid and vapor mole fraction; R_i^j is the molar reaction rate of component i in a reactive unit on stage j ; and V_r^j is the reactive volume on stage j ; k_i^j represents the phase equilibrium constant of component i in the streams leaving stage j ; and h_l and h_v are the liquid and vapor molar enthalpies, respectively.

There is no doubt that the strong coupling among stages and the nonlinearity caused by the chemical reaction leading to difficulties in solving the MESH equations. To overcome these difficulties by PT modeling, Eqs. (3) and (6) are rewritten as differential equations as shown in Eqs. (7) and (8), where the pseudo material holdup M_i^j

and heat holdup H^j given respectively by Eqs. (9) and (10) are introduced to decouple the mass and energy balance equations among stages [37]. M_L^j and M_V^j are the liquid and vapor molar holdups on each stage respectively; C_L , C_V are, respectively, pseudo-holdup coefficients for the liquid and the vapor phases, which are set as 1800 h^{-1} ; and τ_p is set as 1. The GEN term, which is given by $R_i^jV_r^j$ in Eq. (3), is modulated by the continuation parameter α so that the reaction source term on each stage can be eliminated at the beginning of the integration to stabilize the dynamic model.

The resulting PT model of the RD column are summarized as follows:

$$\frac{dM_i^j}{dt} = V^{j+1}y_i^{j+1} + L^{j-1}x_i^{j-1} - V^jy_i^j - L^jx_i^j + \alpha^j R_i^j V_r^j \quad (7)$$

$$i = 1, 2, \dots, Nc; \quad j = 1, 2, \dots, Ns$$

$$\frac{dH^j}{dt} = V^{j+1}h_v^{j+1} + L^{j-1}h_l^{j-1} - V^jh_v^j - L^jh_l^j \quad (8)$$

$$j = 1, 2, \dots, Ns$$

$$M_i^j = M_L^j x_i^j + M_V^j y_i^j \quad (9)$$

$$i = 1, 2, \dots, Nc; \quad j = 1, 2, \dots, Ns$$

$$H^j = M_L^j h_l^j + M_V^j h_v^j \quad (10)$$

$$j = 1, 2, \dots, Ns$$

$$L^j = C_L M_L^j \quad (11)$$

$$j = 1, 2, \dots, Ns$$

$$V^j = C_V M_V^j \quad (12)$$

$$j = 1, 2, \dots, Ns$$

$$\tau_p \frac{d\alpha^j}{dt} = 1 - \alpha^j \quad (13)$$

$$\alpha(t=0) = 0$$

$$y_i^j = k_i^j x_i^j \quad (14)$$

$$i = 1, 2, \dots, Nc; \quad j = 1, 2, \dots, Ns$$

$$\sum_{i=1}^{Nc} x_i^j = 1, \sum_{i=1}^{Nc} y_i^j = 1 \quad (15)$$

$$j = 1, 2, \dots, Ns$$

In the consistent initialization phase, equations on each stage are solved separately from the given initial condition. Over the time integration phase, the equations of all the stages gradually converge to steady state with the coupling effects among stages, and the chemical reaction is gradually introduced.

The PT modeling procedure is similar to the “relaxation” method [38] as it is based on the idea to approach the steady-state through simulating a dynamic process. However, it is a fundamentally different method. Take distillation modeling as an example, the old relaxation method considers the stage hold-ups as constants which results in difficulty in considering the heat balance equation of the MESH model. Otherwise, a high-index DAE system is inevitable. In the PT modeling method, however, the above problems can be avoided by the pseudo-hold-up correlations [37]. The PT modeling method can convert a highly-coupled and strongly nonlinear AE system into a statically-equivalent DAE system.

Until now, a series of unit operation models have been built by many researchers for the purpose of simulation and optimization. The constructed PT models with their references are listed in Table 1.

Table 1

List of established PT models with their references

Unit operation	PT model description	Reference
Flash tank	Pressure-enthalpy flash	[23,25]
Distillation	Equilibrium stage-based model	[23,37]
Reactor	Continuous stirred tank reactor; Equilibrium reactor; gas-phase plug flow reactor	[23,25]
Heat exchanger	Two-stream heat exchanger; Multi-stream heat exchanger; Spiral-wound multi-stream heat exchanger	[23,39,26]
Compressor	Isentropic compressor; Polytropic compressor	[23,28]
Turbine	Isentropic turbine	[23]
Reforming-based hydrogen production plant	High-resolution physics steam-methane reformer model and low-resolution model of other unit operations	[40,41]
Simulated moving bed	Periodic process	[27]
Pressure swing adsorption	Periodic process	[27]
Rate-based packed column	Absorber and stripper of carbon capture process	[42–44]

2.3. Optimization framework with pseudo-transient model

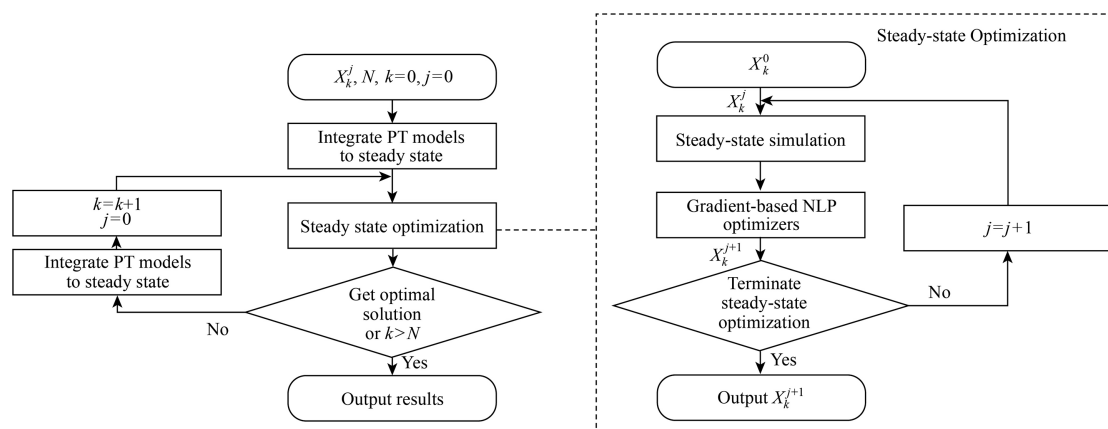
For process optimization using pseudo-transient models, Pattison and Baldea [23] proposed a time-relaxation optimization algorithm [45]. However, such an algorithm has not been commercialized in Aspen Custom Modeler (ACM) and many other EO software, as it is very difficult for most chemical engineers to develop such an algorithm on the platforms provided in commercial software packages. Therefore, Ma *et al.* [37,28] proposed to use a dynamic optimization algorithm as an alternative to the time-relaxation algorithm. However, the dynamic optimization algorithm must solve a sensitivity matrix of process models at each integration step, which is non-trivial and time-consuming. As a result, optimization using such algorithms suffers from low computational efficiency. Furthermore, both the time-relaxation optimization algorithm and the dynamic optimization algorithm conduct dynamic simulations for each optimization step and do not exploit the possibility of performing faster steady-state simulations, which limits the computational efficiency of optimization. To resolve the above problems, Ma *et al.* [46] constructed a steady-state optimization algorithm assisted by pseudo-transient models, which is fast and easy to be interfaced with existing commercial EO software. The algorithm can be briefly illustrated in Fig. 1. In the process of optimization, the algorithm gives priority to steady-state solution in each optimization step instead of the dynamic simulation, and if the steady-state simulation fails, which usually happens in the first several optimization iteration steps, the dynamic simulation using pseudo-transient models is activated to obtain a feasible steady-state solution. This pseudo-transient-model-assisted algorithm is typically more efficient than the time-relaxation-based algorithm as it conducts more steady-state

simulations than dynamic simulations compared to the time-consuming PTC simulations in the time-relaxation-based algorithm. However, for some special complex process, such as hybrid extraction-distillation processes, this optimization framework may fall into less-efficient optimization directions and unnecessarily small step sizes due to frequently failures of steady-state simulations, which would cause more optimization iterations or even failure of the optimization.

The other PT optimization approach is the hybrid steady-state and time-relaxation optimization algorithm, as shown in Fig. 2. The algorithm performs steady-state calculation at first, and only if the steady-state calculation fails to converge, the dynamic simulation is performed to reach a steady state. It should be noted that even though the hybrid steady-state and time-relaxation optimization algorithm is logically robust in convergence, it is hard to be implemented in EO environments since it needs to modify the optimizers in commercial software or even develop a tailor-made optimizer.

To address the above problems, Ma *et al.* [47] developed an improved feasible-path optimization framework containing deliberate solving strategies that switches between steady-state simulations and pseudo-transient simulations to take both advantages of the robustness of pseudo-transient simulations and the efficiency of steady-state simulations respectively, as shown in Fig. 3. In their work, the interaction between the EO modeling environment and the optimization algorithm is achieved via COM interfaces thus offering versatility to the optimization algorithms and easy implementation.

The robustness of the optimization algorithms shown in Figs. 1–3 mainly depends on the employed NLP solvers. A well-known and widely adopted method is sequential quadratic programming (SQP) algorithms, which can only guarantee a local

**Fig. 1.** Steady-state optimization algorithm assisted by PT models.

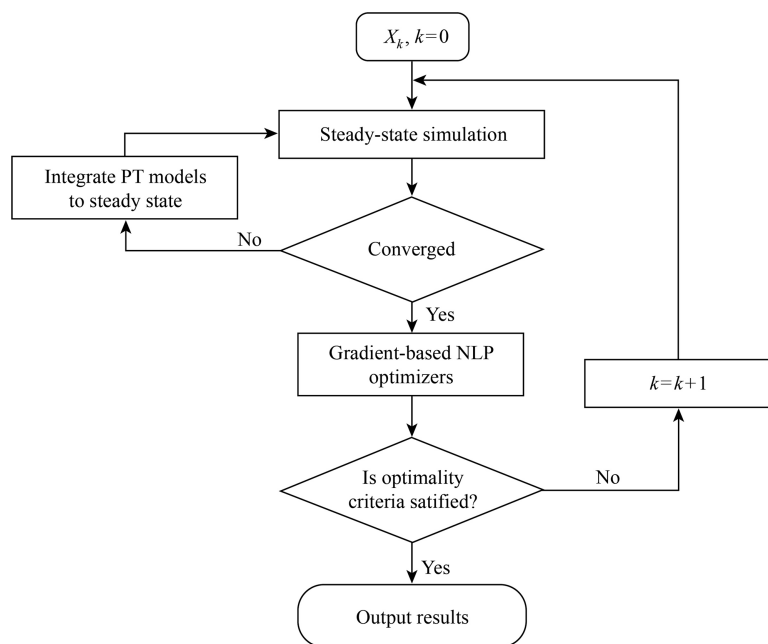


Fig. 2. Hybrid steady-state and time-relaxation optimization algorithms.

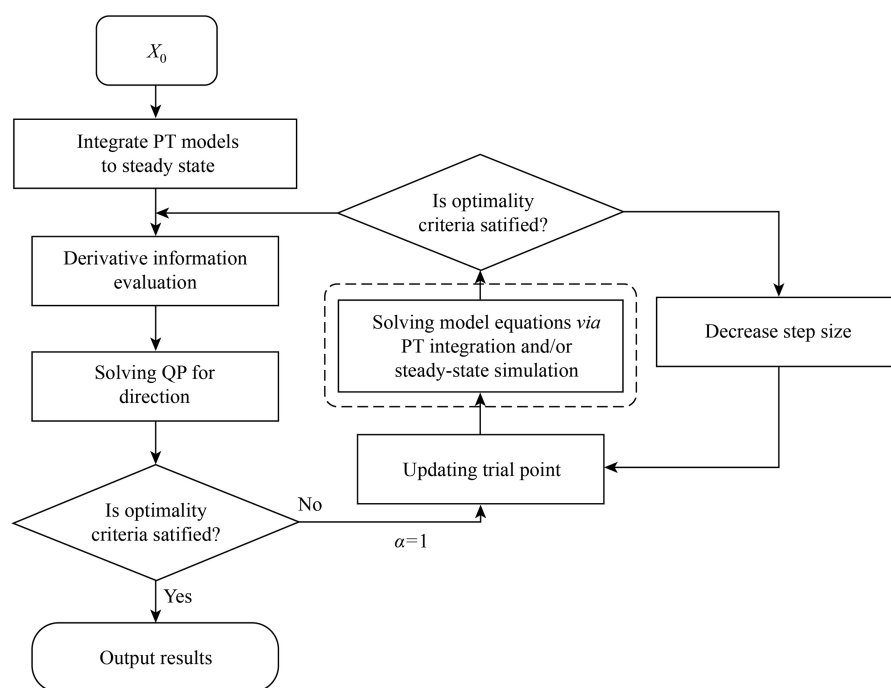


Fig. 3. Improved feasible-path optimization framework.

optimum. To find a better local optimum, almost all research works conduct optimization runs from different initial points.

The pseudo-transient modeling method has been successfully used to simulate and optimize large-scale flowsheets that include complex distillation processes, cryogenic processes, processes with a detailed models, and processes under uncertainty. In the next section, we summarize some main applications of pseudo-transient modeling for solving problems of complex chemical processes optimization.

3. Equation-Oriented Optimization of Complex Chemical Processes Using Pseudo-Transient Models

3.1. Optimization of complex distillation process

In this sub-section, we first describe two types of PT models for distillation with their pros and cons. Then, we present the applications in optimizing complex distillation systems, i.e., the extractive distillation and the dividing wall column (DWC). Next, we present

the development of the original PT model, i.e., the PT reactive distillation model and the PT distillation model considering stage hydraulics. Last, we present the works on the optimal design of distillation sequences.

The economic performance of a distillation column is sensitive to its structural and operating parameters, and a rigorous and reliable method to find optimal values of these parameters in column design is of great importance. Although a great number of studies have been carried out to solve the problem, the rigorous design of distillation columns is still challenging because of the difficulties in effectively solving large-scale nonlinear equation systems.

To resolve this problem, Pattison and Baldea [23] constructed a pseudo-transient distillation model, which was then integrated with the bypass efficiency method proposed by Dowling and Biegler [48,18] to handle the optimization of stage number [35]. However, due to the excessive pursuit of easy initialization, their PT distillation model is complex and not intuitive. Ma *et al.* [37] developed a new PT distillation model based on a simple pseudo-holdup correlation, resulting in a well-posed and easily solved DAE system. Until now, Ma *et al.*'s new PT distillation model has been applied to the optimization of various complex distillation systems, and the dividing-wall column (DWC) and the partially thermally coupled extractive distillation can also be effectively optimized.

Employing the new PT distillation model proposed by Ma *et al.* [37], they successfully optimized a DWC and a partially thermally coupled extractive distillation process, and found for the first time that high purity of the recycle entrainer specification may not be beneficial. Instead, a lower cost can be obtained by compromising the cost of the purification and the recycling quantity of the entrainer. Consequently, they found an optimal solution, wherein the recovered entrainer was not as pure as traditionally assumed but the TAC got lower. Then they successfully optimized distillation systems with heat integration and a heat pump distillation process in the equation-oriented environment [28]. Ma *et al.* [49] optimized a more complex methanol multi-effect distillation system by using the rigorous PT distillation model, and obtained the most economical methanol multi-effect distillation separation process structure and operating parameters.

Taking the new PT distillation model a step further, Ma *et al.* [36] constructed a robust pseudo-transient reactive distillation model, which has been demonstrated its efficiency and robustness by the optimization results. Li *et al.* [50] achieved the simultaneous optimization of distillation systems considering tray hydraulics and revealed that such a consideration could yield reliable operating and structural parameters for real column designs. In their DWC cases [50], the tray pressure drops around the column sections of a DWC are significantly different because of the different hydraulic conditions among the column sections. Therefore, their research suggested that the dividing wall position and the diameters of a DWC should be optimized simultaneously with all the other decision variables to attain a minimum TAC that satisfies the constraints of the products purity requirements, flooding limits, and pressure balance on both sides of the dividing wall.

Moreover, the optimization frameworks with PT models could be integrated with other methods towards distillation sequence synthesis. Hou *et al.* [51] applied the optimization framework to optimize distillation configurations generated by an improved matrix method, achieving a fast and robust distillation configuration generating method based on a rigorous model. For the optimization of a reaction-separation recycle process, Ma *et al.* [52] applied the improved feasible-path optimization framework as an initialization method to obtain a feasible solution.

3.2. Simultaneous optimization of cryogenic processes

Cryogenic processes, such as natural gas liquefaction processes, often contain multi-stream heat exchangers (MHEXs). To realize the simultaneous optimization of such processes, a robust MHEX model capable of handling discontinuity caused by stream phase changes is required. Pattison and Baldea [39] developed a pseudo-transient (simplified) MHEX model by discretizing the exchanger into several enthalpy segments and reformulating the resulting models into DAEs. Two optimization cases, i.e., a standalone MHEX and the Poly Refrigerant Integrated Cycle Operations (PRICO) process, were optimized using the time-relaxation optimization method, demonstrating that the proposed models could facilitate the simultaneous optimization of cryogenic processes containing MHEXs.

Tsay *et al.* [26] then extended the PT modeling method into a detailed spiral-wound multi-stream heat exchange with the unit geometry considered. Based on this detailed unit model, they re-optimized the PRICO process and showed that the optimal designs based on the simplified MHEX model might be suboptimal or even infeasible due to the simplification of the pressure drop calculation and the heat transfer parameter, highlighting the importance of including more detailed process unit models.

3.3. Optimization of process with detailed unit models

The detailed unit model that considers the actual mass- and heat-transfer rate could accurately describe the exact unit operation, however, solving such models is not a trivial work because of the nonlinearity and the size of the resulting partial differential equations. Pattison *et al.* [25] extended the pseudo-transient modeling method into the detailed unit model by fully discretizing spatial domains and then reformulating the resulting equations into pseudo-transient differential equations. In their paper, a detailed gas-phase plug-flow reactor model was developed, and an intensified dimethyl ether (DME) process was optimized. For the convenience of the plantwide optimization, multi-resolution modeling strategy was applied: the reactive systems are represented by multi-scale distributed parameter model, while the separation system is based on MESH equations. The optimization results show vast difference exists between the optimal design with detailed reactive system representation and that with lumped-parameter reactor model, thus highlighting the importance of the detailed unit model.

Motivated by Pattison's work, Kumar *et al.* [40] optimized a reforming-based hydrogen production plant where only the steam-methane reformer was represented as a detailed PT model and obtained optimal process conditions with the goal to maximize the plant thermal efficiency.

Tsay *et al.* [42] constructed a pseudo-transient model for packed absorbers and strippers. They applied this model to optimize the amine scrubbing process, and obtained optimal results with economic potential. Their rate-based column model was then used to represent ionic-liquid-based carbon capture processes to determine optimal process parameters and material-level parameters [43,44].

Similar to the reformulation of detailed unit operation model, Tsay *et al.* [27] developed a pseudo-transient modeling framework for periodic processes comprising the discretization of spatial-temporal domains and the pseudo-transient reformulation. The simulation and optimization results of two periodic processes: a simulated moving bed and a pressure swing adsorption process demonstrated the robustness of the proposed model over the Newton-type solvers.

3.4. Process optimization under uncertainty

Most chemical plants are subject to uncertainties from various sources during operation. Conventional optimization approaches for handling uncertainties require process optimizations for a series of scenarios that approximate the probability distribution of the uncertain parameters. This method scales poorly with the number of uncertain parameters. Alternatively, Tsay *et al.* [53] reformulated the optimization problem as a dynamic optimization problem by representing the uncertain parameters as a set of continuous disturbance variables. With careful design, trajectories of these variables over a pseudo-time domain could efficiently span the uncertainty space. The PT models were applied to alleviate the difficulty in solving model equation systems [53]. Two processes, *i.e.*, a dimethyl ether plant and the Williams-Otto process, were optimized to verify the efficiency of the proposed method. The results showed that this scenario-free method could obtain optimal results similar to the results of the scenario-based method, but with a significant reduction in both CPU time and memory use [53]. Tsay and Baldea [54] then applied this method to optimize the PRICO process to investigate the effect of the feed concentration uncertainty and provided new insights for dealing with uncertainty in the feed composition.

4. Current Challenges and Prospects

This section discusses the challenges and prospects of the PT modeling method in terms of modeling, simulation, and optimization.

Modeling. The pseudo-transient modeling method enables the simulation and optimization based on detailed unit models which accurately predict the actual process, while, on the contrary, the optimization based on the simplified unit models may obtain sub-optimal or even infeasible solutions. As a result, the PT modeling method should be further extended to various detailed unit models, *e.g.*, the rate-based distillation column. Although, for developing a PT-based algorithm, there is no additional assumption over those made for the original steady-state models, for a PT-based method to run well, the PT model must be stable, which should be cared about during the reformulation of the original model.

Simulation. Despite the effort of constructing a fast and robust PT model, the simulation procedure still suffers from the scale and the complexity of the process flowsheet: 1) the PT models reduce the need of deliberate initialization procedures, however, a proper initial point helps to facilitate the PT integration [46], and in some cases, may even be vital; 2) the PT integration requires more computation than the Newton type methods. To improve its efficiency and robustness, various strategies have been proposed. Ma *et al.* [46] proposed a tolerance-relaxation integration strategy where pseudo-transient integrations are carried out multiple times with simulation tolerances decrease gradually from high to low because the integration procedures under higher tolerance are relatively easier and could provide accurate initial points for the following integration procedures. This strategy could save calculation time for 70%–90% and has been integrated with various PT modeling optimization frameworks [46,47,55]. Tsay and Baldea [56] proposed a computationally efficient sequential quasi-steady-state algorithm which enables an efficient transition from pseudo-time integration to the algebraic solution which could save several orders of magnitude of calculation time. However, how to embed this solving method into other commercial modeling environment is still to be resolved.

Optimization. The optimization framework with PT models suffers from the inherent difficulties of the gradient-based optimiza-

tion algorithms. 1) Handling integrality constraints. For the optimization of distillation systems, the stage number introduces integrality constraints. The bypass efficiency method proposed by Dowling and Biegler [48,18] that relaxes the presence or absence of a tray has shown its effectiveness in many distillation processes [35,50]. However, this method is less effective in complex distillation systems, *e.g.*, reactive distillation systems, and often leads to physically infeasible optimal results [36]. 2) Global optimization. The optimization of complex chemical processes is usually nonlinear and nonconvex problems, and the gradient-based optimization algorithms could only guarantee local optima. How to appropriately handle the integrality constraints and how to integrate PT modeling framework with global optimization algorithms call for further research.

5. Conclusions

In this review paper, we presented the state-of-the-art of EO-based methodologies for the optimization problems of complex chemical systems, emphasizing the PT assisted modeling, the simulation, and the optimization framework. By converting unit models into DAE systems that are statically equivalent to the original model, the solution of the resulting models could be obtained via the consistent initialization and the pseudo-transient integration. Compared with the conventional Newton type method, the PT modeling method has a much larger convergence basin. Several optimization frameworks were also described. Here we recommended steady-state optimization based on pseudo-transient models and improved feasible path optimization frameworks for easy-implementation. Then we showed various applications of the proposed method, *i.e.*, complex distillation processes, cryogenic processes, processes with detailed unit models, and processes under uncertainty. The successful optimization of many challenging chemical processes indicated EO-based methods may hopefully become a promising approach toward the rigorous optimization of large-scale and complex chemical processes. Finally, the review described the current challenges and prospects of the PT modeling method.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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