

Optimization of Periodic Adsorption Processes with a Novel Problem Formulation and Nonlinear Programming Algorithm

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Periodic Adsorption Processes (PAPs) have gained increasing commercial acceptance as efficient gas and liquid separation techniques. Applications cover a broad range from air separation, purification of hydrogen from refinery gases to purification of enantiomeric compounds for pharmaceutical products. PAPs are based on solid-fluid equilibrium and are generally no more complex than most conventional separation processes. However, they differ in one essential feature: the process operates under periodic transient conditions, whereas most processes such as absorption, extraction, and distillation operate steady-state conditions. Models for PAPs are therefore multiple instances of PDEs in time and space with periodic boundary conditions that link the processing steps together. As a result, the optimization of such systems for either design or operation represents a significant challenge to current DAE solution and nonlinear programming algorithms.

This study considers a simple application of PAPs that illustrates a novel nonlinear programming strategy for the optimal design and operation PAP systems. The approach incorporates the use of automatic differentiation for deriving the first and second order adjoint profiles as well as the Hessian/vector product to maximize the product recovery of a PAP process at desired purity. In addition, a trust region method is developed to solve the resulting nonlinear program with specialized quasi-Newton methods that calculate the normal and tangential steps. Results on this example demonstrate tremendous potential over previous studies with reduced Hessian SQP approaches, and point the way to more complex applications.

Extended Description

Periodic adsorption processes (PAPs) consist of vessels or beds packed with solid sorbent. The sorbent is contacted with a multicomponent fluid feed to preferentially adsorb one of the chemical components onto the solid. Examples of these processes include vacuum swing adsorption to separate oxygen from air, pressure swing adsorption to separate hydrogen from hydrocarbons in refinery gases, and simulated moving bed chromatography to separate two enantiomers (e.g., glucose and fructose) in a liquid phase. PAPs are typically operated in a cyclic manner with each bed repeatedly undergoing a sequence of steps. For gas-solid adsorption typical steps include *pressurization*, *adsorption*, *blowdown*, *desorption* and *pressure equalization*. Within each step

equilibrium and mass transfer processes occur as a result of contact between the fluid and solid phases. This leads to concentration (and also temperature and pressure) waves that move through the bed, often with steep fronts.

Development of PAPs relies on the following three tasks. First, an accurate model representation must be developed for the micro-scale adsorption process, the transport model for the adsorption bed and the overall flow pattern between beds. This task requires a strong understanding of the adsorption phenomenon as well as heat, momentum and mass transfer models, and is a necessary prerequisite to an accurate simulation tool. The second task deals with the development of specialized algorithms for solving PAP bed models. The behavior in each bed is described by partial differential equations in space and time, constructed from conservation of heat, mass and momentum augmented by transport and equilibrium equations. In this study, we will focus on the popular linear driving force (LDF) model with hyperbolic PDAEs, as it offers a realistic representation of industrial processes as well as a good compromise between accurate and efficient solutions of these models. A summary of these bed equations is given below.

a) Mass balance	$\varepsilon_B \frac{\partial \rho_i}{\partial t} + \rho_s \frac{\partial n_i}{\partial t} + \frac{\partial (\rho_i v)}{\partial z} = 0$	$i = 1, 2, \dots, N_c$
b) Mass transfer	$\frac{\partial n_i}{\partial t} = \frac{k_i}{R_{pv} T} (p_i - p_i^*)$	$i = 1, 2, \dots, N_c$
c) Energy balance	$\left(\varepsilon_B \sum_{i=1}^N \rho_i (c_p^i - R_E) + \rho_s c_s + \rho_s \sum_{i=1}^N n_i c_p^i \right) \frac{\partial T}{\partial t} - \rho_s \sum_{i=1}^N q_i \frac{\partial n_i}{\partial t} + \frac{\partial (v h)}{\partial z} = 0$	
d) Steady State momentum balance (Ergun Equation)	$-\frac{\partial P}{\partial z} = 150 \frac{\mu v}{d_p^2} \frac{(1 - \varepsilon_B)^2}{\varepsilon_B^3} + 1.75 \frac{\rho M v^2 (1 - \varepsilon_B)}{d_p \varepsilon_B^3}$	
e) Dual-site Langmuir Adsorption Isotherm	$n_i^* = m_1 \frac{b_i P_i^*}{1 + \sum_{j=1}^N b_j P_j^*} + m_2 \frac{d_i P_i^*}{1 + \sum_{j=1}^N d_j P_j^*} \quad \text{where } b = b_0 \exp\left(\frac{q_i}{R_E T}\right) \text{ and } d = d_0 \exp\left(\frac{q_i}{R_E T}\right)$	
Gas in the macro pores of the adsorbent	$poregas = (\varepsilon_T - \varepsilon_B) \rho_i / \rho_s \quad \text{and } n_i = n_i^* + poregas$	
Ideal gas law	$\rho = P / (RT)$	
Enthalpy	$h = \sum_i \rho_i (aT + bT^2 + c_{p,C}^i T^3 + c_{p,D}^i T^4)$	
Molecular weight	$M = \sum_i y_i M_{0,i} \quad \text{where mole fraction } y_i = \rho_i / \rho$	
Fluid viscosity	$\mu = \sum_i \mu_i y_i \quad \text{where } \mu_i = \mu_{0,i} + \mu_{1,i} T$	

The third task relates to the simulation of the PAP cycle and consideration of the optimal performance of PAP steps. Cycle models consist of the bed models, partial differential equations (PDEs) in time and space, solved for each adsorption step. After a relatively brief startup period, the adsorption beds run in a cyclic steady state (CSS), that is, the bed conditions at the beginning of each cycle match those at the end of each cycle. This task

is essential for the design of adsorption processes since reliable and efficient algorithms are key prerequisites to evaluating proposed designs, analyzing processes for safety, controllability and operability, debottlenecking and retrofitting existing units, and optimization of new designs or existing installations. Moreover, the synthesis and evaluation of new adsorbents clearly benefits from these tools and efficient PSA simulations have replaced many expensive and time consuming laboratory studies and allow the rapid evaluation of innovative and creative designs. This study extends these developments and focuses on optimization of PAP systems. The optimization problem based on CSS of PSA systems can be expressed as:

$$\begin{aligned}
& \text{Min } \phi(y, y_0, q) \\
& \text{s.t. } F_1(y_1, y_1', q, t) = 0, \quad y_1(t_0) = y_0, t \in [t_0, t_1] \\
& \quad F_i(y_i, y_i', q, t) = 0, \quad y_i(t_{i-1}) = y_{i-1}(t_{i-1}), t \in [t_{i-1}, t_i], i = 2, \dots, N \\
& \quad W(y(t), y_0, q) \leq 0 \\
& \quad C(y_0) = y_0 - y_N(t_N) = 0 \\
& \quad LB \leq (y_0, q) \leq UB
\end{aligned} \tag{1}$$

Here the bed models in the table are discretized in space using the method of lines and posed as a set of DAEs for step i . We define y as the combined vector of state variables after spatial discretization, y_0 are initial conditions for the state variables, q are decision variables and both are subject to the lower bounds (LB) and upper bounds (UB), W are design constraints (posed here as inequalities) which can include purity, pressure or production rate requirements and C are the CSS conditions. Candidates for q can be geometric parameters such as bed length, diameter and adsorbent packing or process parameters such as flow rates, step times and operating pressures. Finally, ϕ is the objective function and can be:

- Maximize overall recovery at desired purity
- Maximize profit at desired purity
- Minimize work/power usage at desired purity

Typical optimization applications are cycle design, parameter estimation of adsorbent properties, optimization of operating conditions and online optimization.

To solve problem (1) we apply an optimization strategy based on an SQP approach after implicitly eliminating the DAEs and the state variables $y(t)$. In the absence of inequality constraints, the SQP method can be observed as Newton's method applied to the KKT conditions of (1). The Newton step at iteration k can be written as:

$$\begin{bmatrix} B_k & A_k^T \\ A_k & 0 \end{bmatrix} \begin{bmatrix} d_x \\ d_\lambda \end{bmatrix} = - \begin{bmatrix} \nabla L(x_k, \lambda_k) \\ c(x_k) \end{bmatrix} \tag{2}$$

where x is defined as $x^T = [y_0^T q^T]$, $A_k = \nabla C(x_k)^T$, B_k is the Hessian of the Lagrange function ($L(x, \lambda) = \phi(x) + c(x)\lambda$) or its approximation. In previous work (Ling et al., 2003) a reduced Hessian SQP approach was applied which leads to a decomposition of (2) where A_k was calculated from a direct sensitivity approach applied to the DAE system and the reduced Hessian related to B_k is created by quasi-Newton updates. Solution of the

optimization problem indicates that significant improvements are possible with modest computational effort. However, the bottleneck to more efficient calculation is the evaluation of direct sensitivities to obtain A , which is a dense matrix.

This study develops a new nonlinear programming approach with A and B in (2) constructed via quasi-Newton updates (TR1) and (SR1) described in Griewank and Walther (2002). The terms on the right hand side of (2) are evaluated exactly using an adjoint approach for the DAE model. Globalization of the resulting nonlinear programming algorithm is provided by a composite step trust region approach with tangential and normal steps related to (2) and calculated on the approach of Byrd and Omojukun (see Nocedal and Wright, 1999).

The implementation of this optimization strategy is described using CVODES, ADOL-C and a trust region variant of the STR1 algorithm. After converting the PDEs to DAEs, we apply the DAE solver CVODES (Hindmarsh and Serban, 2002) to integrate the bed equations, and to apply an adjoint method from final time to initial time in order to construct the desired gradients. We also compute the sensitivities right hand side using automatic differentiation ADOL-C 1.8.7 (Griewank and Juedes, 1999), to provide accurate sensitivities. The overall optimization strategy is illustrated for a small three step adsorption process for the separation of air. In the full paper we present complete numerical results and compare this approach to an reduced Hessian SQP method where A is calculated exactly with a direct sensitivity method (using DASPK). The new approach shows a significant reduction in computing resources and shows great potential for extension to larger problems.

References:

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