

# AN OVERVIEW ON CONVERGENCE ACCELERATION OF CYCLIC ADSORPTION PROCESSES

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## ABSTRACT

Cyclic adsorption processes are inherently dynamic where the process variables are always varying with time. The cyclic processes have no steady state. Thousands of repeated cycles may be needed before cyclic steady state (CSS) is reached. In this paper, the basic concept and characteristics of cyclic adsorption processes are first introduced, using air separation by rapid pressure swing adsorption as an example. Next, different approaches to calculate and accelerate the convergence of CSS are briefly reviewed. The computational time can be reduced by having an efficient discretisation technique and accelerators to achieve the final CSS. Hybrid methods are potentially attractive.

**Keywords:** Adsorption, Convergence Acceleration, Cyclic Process

## 1.0 INTRODUCTION

The phenomenon where the gas molecules form bonds with the surface of a solid and become attached is termed as adsorption. The reverse process where the adsorbed molecules are removed from the solid surface is called desorption or regeneration. A complete operation of adsorption and desorption is called cyclic adsorption process. In a physical cyclic adsorption process, there are a few methods to regenerate the saturated bed, e.g.: Pressure Swing Adsorption (PSA) where the bed regeneration is accomplished by reducing the total pressure of the adsorber; Vacuum Swing Adsorption (VSA) where partial pressure is reduced; Temperature Swing Adsorption (TSA) where the temperature is increased. The application of these cyclic adsorption processes has been employed in many important separations such as air separation, carbon dioxide recovery from combustion process, trace volatile organic component removal, hydrogen recovery from refinery gases, air drying, separations of olefins and paraffins, and many more novel separations in the fine chemistry industry.

A unique feature of cyclic process is that it has no steady state. After some repeated cycles, cyclic steady state (CSS) is achieved. The computational load for the calculation of CSS is usually heavy. The objectives of this paper are:

- to illustrate the concept and basic characteristics of cyclic adsorption processes, and
- to provide an overview on approaches proposed in the literature for accelerating the calculation of the CSS. Possible improvements are also suggested.

## 1.1 Cyclic adsorption model

The transient cyclic adsorption process can be modeled by using partial differential equations (PDEs) for mass conservation in the fluid phase, ordinary differential equations (ODEs) for the sorption rate in the stationary phase, and algebraic equations for the adsorption equilibrium between phases.

Overall material and component balances for fluid phase:

$$\varepsilon_b \frac{\partial c}{\partial t} = -\frac{\partial(uc)}{\partial z} - \sum_i R_i \quad (\text{Equation 1})$$

$$\varepsilon_b \frac{\partial c_i}{\partial t} = -\frac{\partial(uc_i)}{\partial z} + \frac{\partial}{\partial z} \left( D \frac{\partial c_i}{\partial z} \right) - R_i \quad (\text{Equation 2})$$

where  $R_i$  is the uptake rate of component  $i$  by the particles per unit volume of the bed ( $\text{mol m}^{-3} \text{s}^{-1}$ ),  $D$  is the dispersion coefficient,  $\varepsilon_b$  is the bed porosity. Depends on the adsorption kinetics of the system, the sorption rate in the stationary phase varies. The value of  $R_i$  therefore depends on mass transfer resistance of the model. The uptake rate is commonly approximated using linear driving force (LDF) model

$$R_i = \rho_b \frac{\partial \bar{q}}{\partial t} = k (q^* - \bar{q}) \quad (\text{Equation 3})$$

where  $\rho_b$  is the bed density,  $q^*$  is the adsorbed phase concentration at equilibrium,  $\bar{q}$  is the average adsorbed phase concentration over an entire particle volume, and  $k$  is the LDF mass transfer coefficient.

At equilibrium, the adsorbed phase concentration is often expressed as a function of the concentration of fluid phase:

$$q^* = f(c) \quad (\text{Equation 4})$$

### 1.2 Definition of CSS

The nature of cyclic adsorption process has no steady state like general continuous process, it is inherently dynamic. Once the cyclic process is initiated, the process undergoes a transient stage prior to reach CSS. An adsorption cycle can be viewed as an orbit as shown in Figure 1. With initial vector that composed of process states variables in the model equations,  $\bar{X}_0$ , the cycle transforms the initial vector to a new vector,  $\bar{X}_n$  at the end of the cycle. When the new vector completely specify the state of the bed at the beginning and end of the cycle,  $\bar{X}_e$ , CSS is reached and the process will repeatedly continue as a prefixed orbit (Croft and LeVan, 1994). At CSS, the process state variables at some instant within a cycle have the same value at the corresponding instant within each subsequent cycle (Choong, 2000).

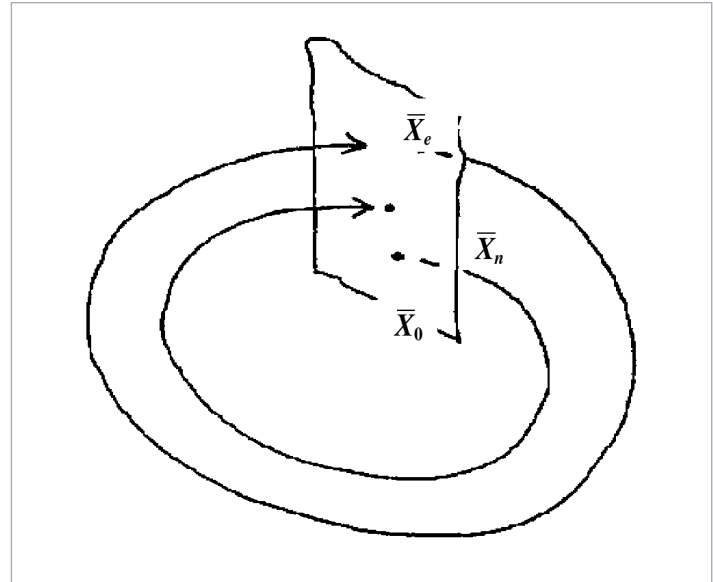


Figure 1: Depiction of an adsorption cycle

To illustrate the behavior of various process state variables at CSS, an isothermal Rapid Pressure Swing Adsorption (RPSA) model for air separation using zeolite 5A as adsorbent was used. Details of the process description can be found in Choong (2000). It is shown in Figures 2 and 3 that the process state variables, *e.g.* total pressure and oxygen mole fraction at some instant within a cycle have almost the same values at the corresponding instant within each subsequent cycle. CSS is reached and both the total pressure and oxygen mole fraction oscillate with time about a mean value as shown in Figures 4 and 5.

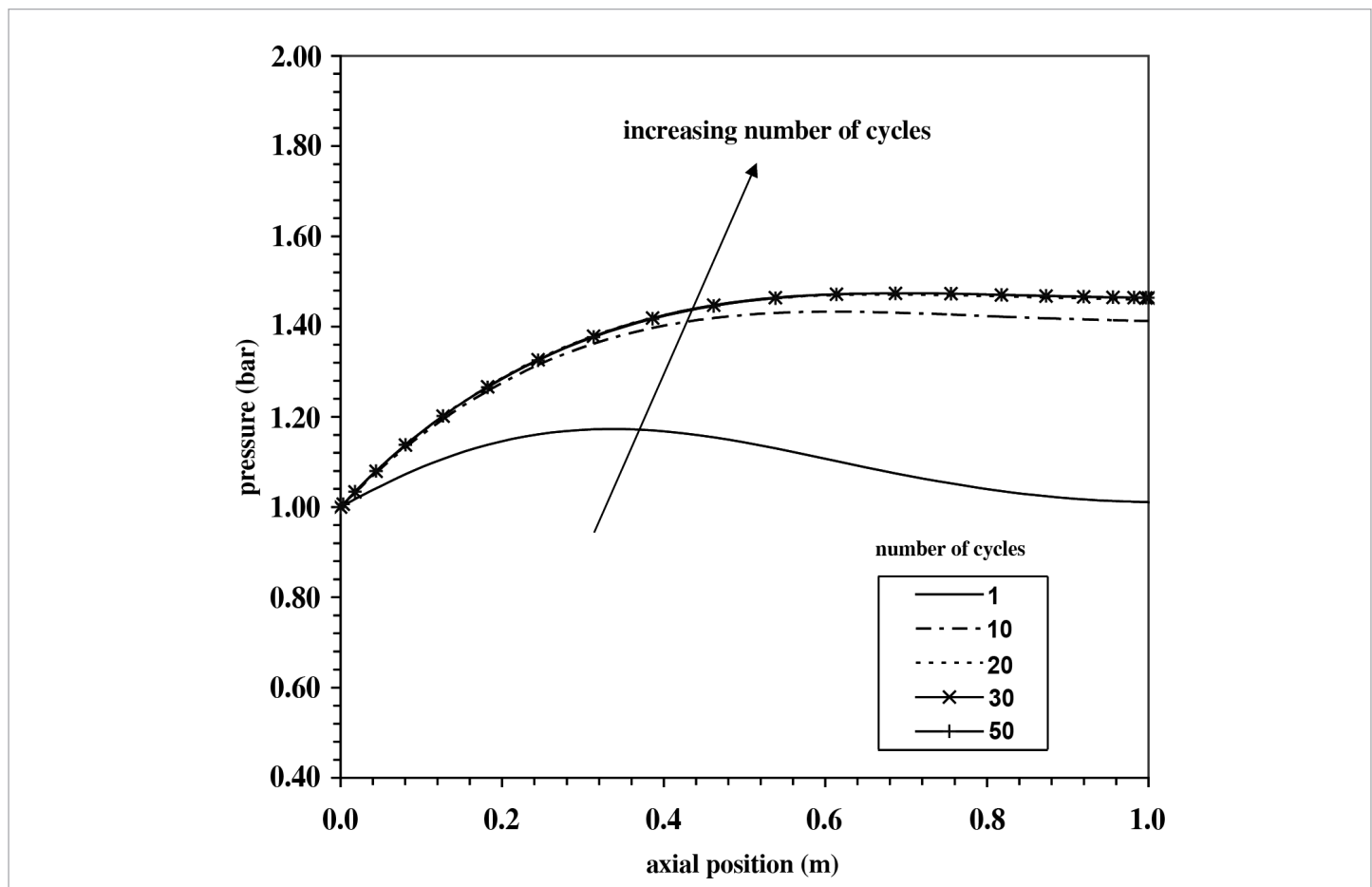


Figure 2: Total pressure at the end of the depressurisation step as a function of axial position after various numbers of cycles (Choong, 2000)

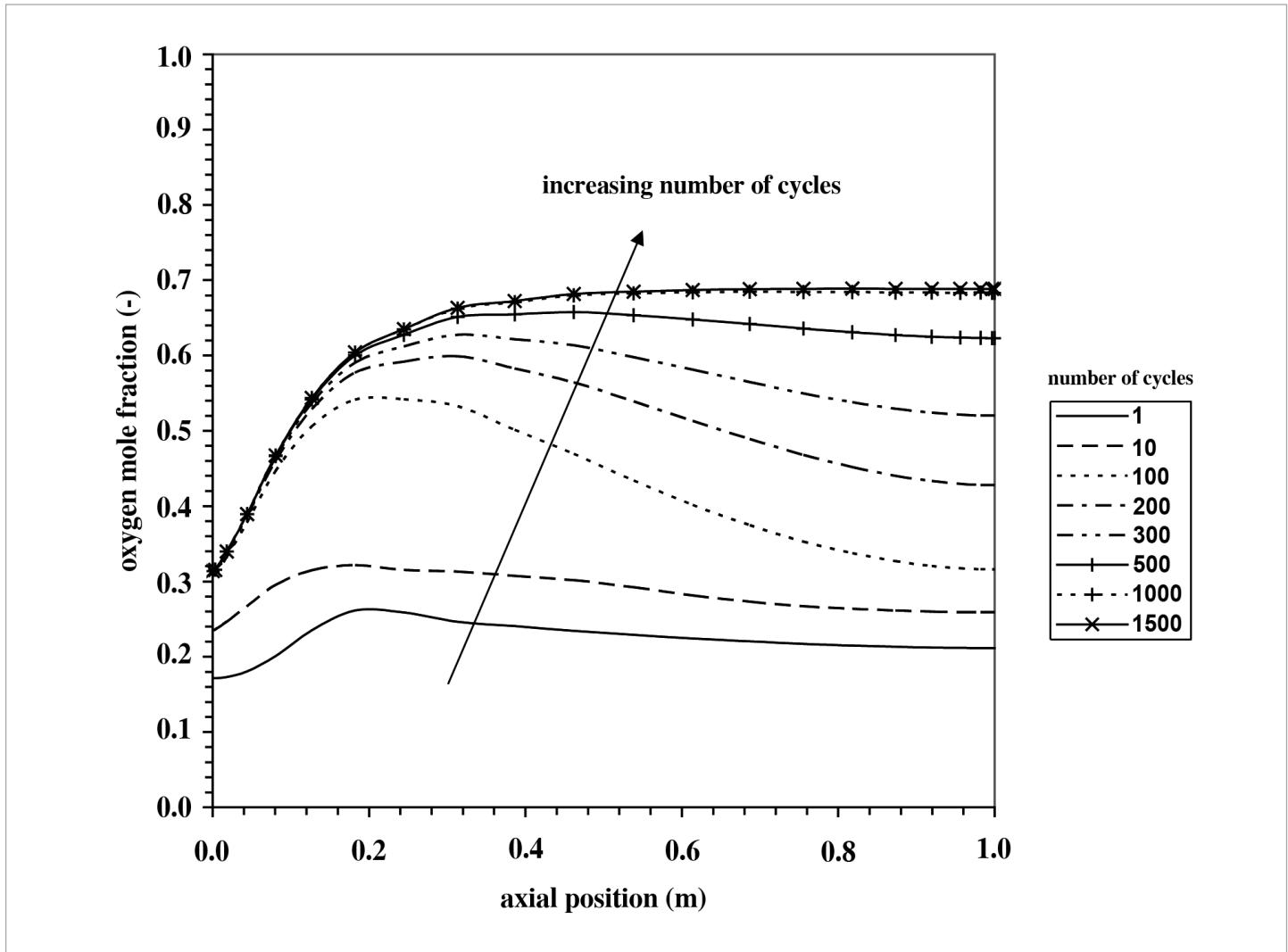


Figure 3: Oxygen mole fraction at the end of the depressurisation step as a function of axial position after various numbers of cycles (Choong, 2000)

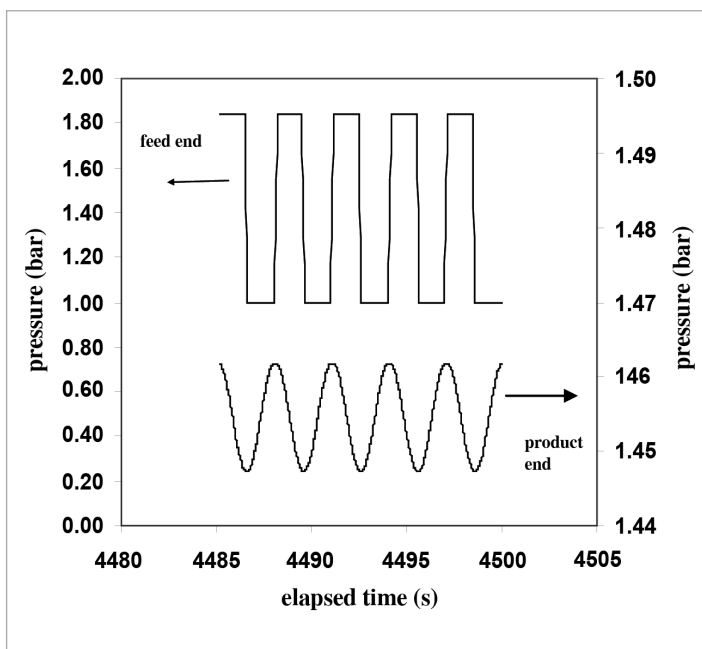


Figure 4: Total pressure at the feed end and product end of the bed as a function of time at CSS (Choong, 2000)

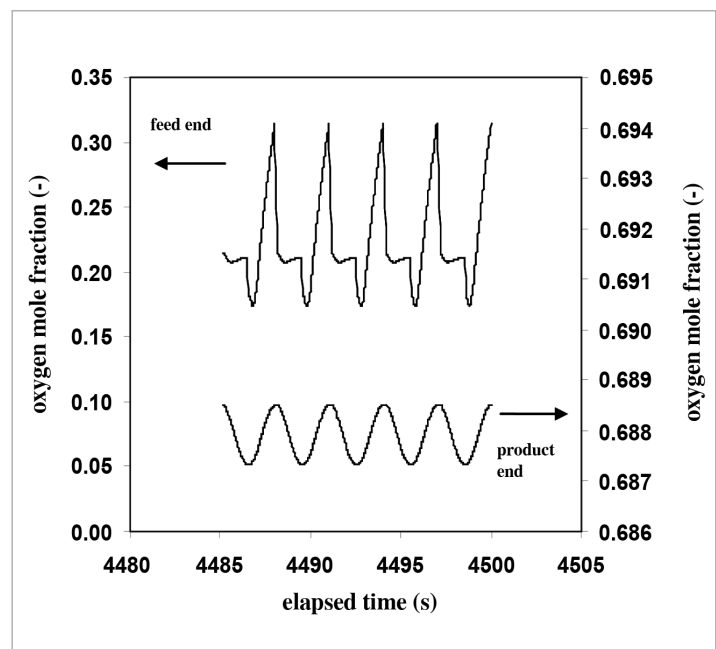


Figure 5: Oxygen mole fraction at the feed end and product end of the bed as a function of time at CSS (Choong, 2000)

## 2.0 APPROACHES AND CONVERGENCE ACCELERATION TO CALCULATE CSS

The most commonly approach to calculate CSS is the dynamic simulation where the simulation follows the dynamics of the real process. Mathematically, this is the Method of successive substitution (MSS). The calculation involves a series of complete cycle with the results of the previous cycles will be used as initial conditions for the next cycle. This is the preferred method if the process dynamics of the simulation are important.

Depending on the systems considered, hundreds or thousands of cycles may be required to achieve CSS using the method of MSS (Choong, 2000), and therefore this may be computationally demanding. Reduction of computational time may be achieved by (i) improving the numerical methods used to solve the model equations, *e.g.* discetisation techniques (ii) speeding up the convergence of CSS, *e.g.* accelerated MSS and direct determination. Figure 6 shows a summary on the approaches and convergence acceleration to calculate CSS.

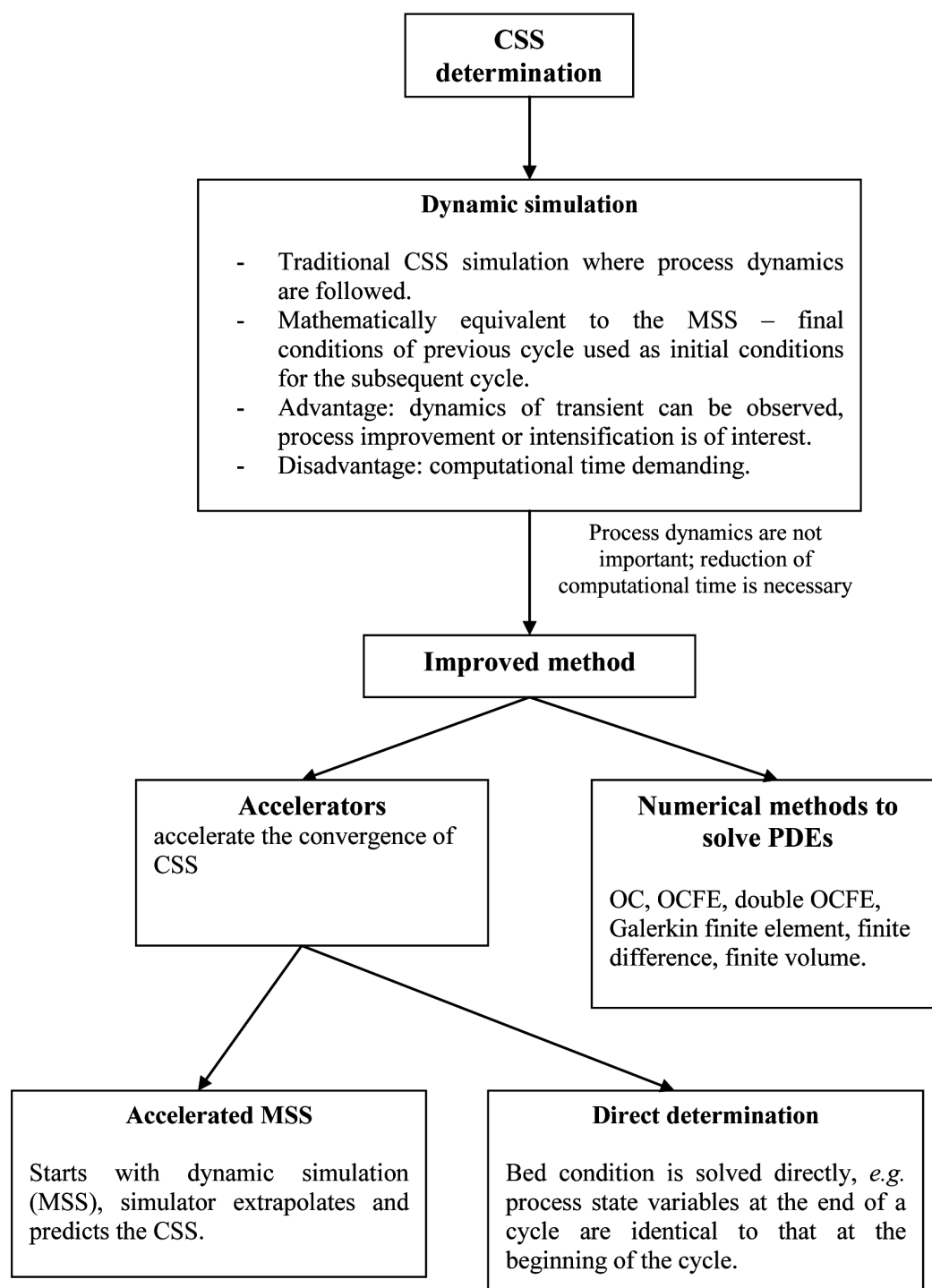


Figure 6: Summary of approaches and convergence acceleration to calculate CSS

## 2.1 Numerical methods to solve model equations (Discretisation techniques)

In general, there are two approaches to solve the model equations:

- (i) complete discretisation where the PDEs are discretised with respect to both time and space domain (Nilchan and Pandelides, 1998; Raghavan and Ruthven, 1985), resulting in a system of simultaneous algebraic equations;
- (ii) spatial discretisation or the method of lines where the PDEs are first spatially discretized into ODEs in the space domain. The system of ODEs is then solved by appropriate numerical integrator.

There are a few type of numerical methods used to discretize the PDEs: orthogonal collocation, OC (Hassan *et al.*, 1987; Raghavan *et al.*, 1985), orthogonal collocation on finite element, OCFE (Alpay, 1992; Da Silva *et al.*, 1999), Galerkin finite elements (Teague and Edgar, 1999), finite difference method (Ko and Moon, 2000), finite volume method (Cruz *et al.*, 2005; Webley and He, 2000). The OC method is the most commonly used spatial discretisation in the simulation of cyclic adsorption processes. It is demonstrated by Hassan *et al.* (1987) that the OC method was substantially more efficient than finite difference method for cyclic adsorption problems. In terms of computing time, conclusion was made by Alpay (1992) that OCFE was the most efficient method among OC, OCFE, double OCFE and cell-in-series for RPSA models. It is also showed by Webley and He (2000) that the finite volume method with appropriate extrapolation was flexible to accommodate boundary conditions for any type of cycle relevant operation.

## 2.2 Accelerators

In context of this paper, accelerators refer to the simulator that can accelerate or speed up the convergence of CSS. Accelerator is often used when the information on the transient is not important or process optimisation is of interest. Two types of accelerators are discussed in this section:

- (i) accelerated MSS and
- (ii) direct determination. Accelerated MSS starts with MSS for the first few cycles. The simulator then extrapolates and predicts the final CSS. As for direct determination, the state variables of two cycles are set to be the same between two subsequent cycles and solved by incorporating the boundary conditions at both ends of the adsorption column.

### 2.2.1 Accelerated MSS

Kvamsdal and Hertzberg (1997) investigated two accelerated MSS methods, namely Aitken and Muller methods. It was found that both methods reduced the number of cycles calculated to converge to CSS. However, in order to obtain the same CSS profile by the traditional MSS, they had to tune the error tolerance used in the stopping criterion of their accelerators.

Choong *et al.* (2002) recommended that the MSS can be supplemented with extrapolators that accelerate convergence to CSS. The effectiveness of this method was demonstrated using both the simulation of RPSA. Under suitable conditions, the paired extrapolators approach CSS from opposite sides, thus effectively bracket the CSS. The technique of paired extrapolators reduces the number of cycles to reach CSS by 300%. The reduction of computing time achieved by the extrapolators may not be as large

as reported by some of the accelerators in the literature. However, the improvement reported is often measured with respect to MSS without a reliable criterion for identifying CSS. Furthermore, the accelerators in the literature may not converge to the exact CSS (*e.g.* Nilchan, 1997) as the extrapolators developed by Choong *et al.* (2002) do.

Lübke *et al.* (2006) proposed a new algorithm, namely cascading algorithm to shorten the computational time of determining the CSS of simulated moving bed processes by approximating the CSS on a coarse space-time mesh first and then using the rough approximation as the initial condition on the finer mesh. Complete discretisation was adopted in this algorithm. The algorithm starts with calculating the CSS with initial condition for the first level. In case that the space grid of the next level does not coincide with the previous level, linear interpolation from the coarse to the refined grid is used. A considerable reduction in computational time was achieved.

### 2.2.2 Direct Determination

The direct determination method solves directly for the bed condition that at the end of a cycle that is identical to that at the beginning of the cycle, giving the desired periodicity requirement (Ding *et al.*, 2002). Croft and LeVan (1994) used Newton method to speed up the convergence rate of a PSA process. The method gave considerable reduction in number of iteration but the computational time increased correspondingly. Ding and LeVan (2001) further enhanced the direct determination of Croft and LeVan (1994) by introducing a hybrid method of Newton and Broyden to reduce the calculation of Jacobian matrix in conjunction with a novel iterative-secant approach to increase stability and to avoid the calculation of the first Jacobian matrix for the hybrid Newton–Broyden method; implemented a sensitivity interpolation technique with dynamic grid allocation; and specified a dynamic integration error tolerance. Using an isothermal trace separation PSA process as a case study, the enhanced formulation resulted in 40 times faster than the original formulation proposed in by Croft and LeVan (1994) and 100 – 1000 times faster than the successive substitution method. However, the comparative computational cost of the increasing number of nodes in the spatial discretisation as compared to the MSS was not very clear.

Kvamsdal and Hertzberg (1997) also investigated the efficiency of direct determination on calculating the convergence of CSS by using Broyden and damped Newton-based approach. Comparisons were made between the two methods, the accelerated successive method (Aitken and Muller) as well the traditional MSS. It was found both the direct determination methods took longer calculation time than the traditional MSS although the number of cycles calculated to converge to CSS has been reduced tremendously. Between the two direct determination methods, Broyden's method needs shorter calculation time as this method does not require Jacobian matrix to be calculated at every iteration as the damped Newton-based approach.

Van Nordeen *et al.* (2002) introduced a hybrid convergence method called the Newton-Picard method for cyclically operated reactors and separators. This method combines the strong points of dynamic simulation and the Newton's method. The hybrid method is based on the decomposition of the state space and is also to compute the eigenvalues that determine the stability of a periodic state. They applied the proposed method into three



non-linear systems ( $\text{CO}_2/\text{N}_2$  PSA,  $\text{H}_2\text{S}$ /natural gas PSA and reverse flow reactor) and two linear systems ( $\text{H}_2\text{O}$ /air PSA and  $\text{CO}_2/\text{He}$  PSA). For the non-linear systems, they compared the Newton-Picard method to three existing method: MSS, Newton's method and Broyden's method. The results were that only for the  $\text{CO}_2/\text{N}_2$  PSA separation, the Newton-Picard converged relatively slower than MSS. The method was in most cases much more efficient than MSS or Newton's method. For the linear systems, they investigated which method was the most appropriate to compute CSS. They demonstrated that when the largest eigenvalue of the Jacobian matrix of a linear system and the dimension of the system is known, it is possible to decide beforehand whether Newton's method or MSS will be more efficient to calculate the CSS. For both linear and non-linear systems, Broyden's method was found to be most efficient in terms of number of cycles required

although it suffered from robustness problems in non-linear cases. Nevertheless, in situation where the stability of periodic states was needed, the Newton-Picard method was superior to Broyden's method because the Newton-Picard method computes approximations to the eigenvalues that determine the stability of the periodic states.

## 4.0 CONCLUSION

The convergence acceleration of CSS can be achieved either by using efficient PDE solvers or by devising efficient accelerators. A brief but comprehensive survey on the convergence acceleration of CSS has been presented. It appears that a hybrid method is particularly attractive. Our research group is now working on devising efficient hybrid method for the acceleration of the convergence of CSS. ■

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