Preprints of the
9th International Symposium on Advanced Control of Chemical Processes
The International Federation of Automatic Control
June 7-10, 2015, Whistler, British Columbia, Canada

Optimization of the Cyclic Operation of a Continuous Biobutanol Fermentation Process Integrated with Ex-Situ Adsorption Recovery

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Abstract: Biobutanol has received significant attention as a renewable gasoline substitute and as a chemical feedstock owing to its high energy content, low volatility, and low water solubility. Low volumetric productivity caused by the toxicity of butanol in batch fermentation stands as one of the major obstacles to the commercialization. In this paper, continuous biobutanol fermentation with ex-situ adsorption recovery of butanol is investigated as a way to overcome this limitation. In this integrated system, the spatial segregation of the adsorption system and the fermentation process enables continuous biobutanol production without the need to stop the fermentation. Since the adsorption column needs to be switched periodically owing to the limited capacity of the adsorbent, the overall operation follows a cyclic pattern and the fermentation process converges to a cyclic steady state (CSS). In this study, a dynamic model of the integrated process is constructed and used for dynamic simulation to determine the system. Major operating variables are optimized through grid search for given feed concentrations based on the predicted CSS behavior in order to design an operation strategy that satisfies given requirements.

Keywords: Continuous biobutanol fermentation; Ex-situ adsorption recovery; Monod model for fermentation kinetics; Cyclic steady state; Grid search optimization

1. INTRODUCTION

Biobutanol has received significant attention, not only as a renewable gasoline substitute but also as a chemical feedstock for butyl acrylate, butyl acetate, glycol ether and etc. (García et al., 2011, Green, 2011). Its main advantages over bioethanol, the other popular renewable fuel, are high energy content, low volatility, and low water solubility. Biobutanol is produced from the fermentation of sugar derived from various biomass; Acetone-Butanol-Ethanol (ABE) fermentation by *Clostridia* is one of the oldest industrial processes for butanol production.

However, the traditional ABE batch fermentation suffers from low productivity as the microorganism's cell growth and therefore the butanol production become inhibited when the butanol concentration in the bioreactor reaches above the level of 13~20g/L. The toxicity of butanol causes complications such as low product (ABE) yield (<35%), low volumetric productivity (<0.5g/L·hr), and low product concentration (< 20 g/L) in the broth leading to high recovery costs (Green, 2011, Kumar and Gayen, 2011, Tashiro and Sonomoto, 2010). This stands as one of the biggest obstacles to making biobutanol commercially feasible.

One of the suggested ways to overcome the limitation by the butanol toxicity is to remove the produced biobutanol from the broth while the fermentation is on-going, so as to maintain the butanol concentration below the threshold of toxicity. For recovering the butanol from the broth, traditional separation methods like the distillation is not suitable as it can consume much energy - even more than that contained in the product. Many alternative recovery technologies have been investigated for integration with the biobutanol fermentation process, including adsorption, liquid–liquid extraction, gas stripping, pervaporation, perstraction, and reverse osmosis (Ezeji and Li, 2010, Vane, 2008). Among them, adsorption is considered to be the most attractive due to its simplicity and relatively low energy requirement (Oudshoorn et al., 2009, Qureshi et al., 2005).

There are two ways to integrate adsorption with fermentation: the *in-situ* recovery and the *ex-situ* recovery. In the former, adsorbents with high selectivity for butanol are added directly to the bioreactor, and both the fermentation and the adsorption occur in single batch bioreactor (Fig. 1A) (Groot and Luyben, 1986, Qureshi et al., 2005). Due to the batch nature, the fermentation needs to be stopped once the adsorbents become saturated. The latter option involves a system composed of two parts: a bioreactor and an adsorption column filled with absorbents which have high selectivity for butanol (Fig. 1B). As the column can be switched with a new one upon saturation, it allows for a continuous fermentation processing without the need to stop the fermentation and thus can raise both yield and productivity significantly.

In continuous biobutanol fermentation with the ex-situ adsorption recovery, since the adsorption column has to be switched periodically owing to the limited capacity of the adsorbent, the overall operation follows a cyclic pattern and the fermentation process converges to a dynamic behaviour that is repeating, the so called *cyclic steady state (CSS)*. The CSS condition is important as it can serve as the basis for optimizing the design and operation of what is inherently a dynamic process. This research aims to provide insights into

design and optimization strategies for the continuous biobutanol fermentation process based on the CSS analysis.

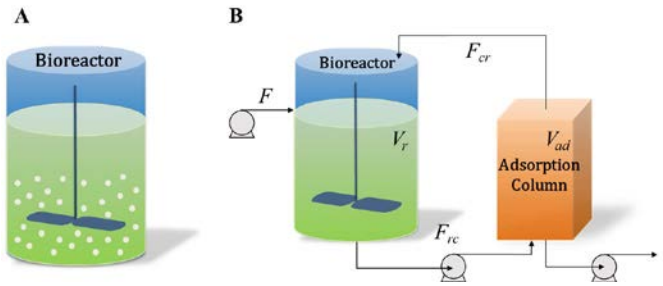

Fig. 1 A diagram of recovery processes by adsorption. A) In-situ recovery process, B) Ex-situ recovery process.

In this study, a dynamic model of the integrated process is constructed and used for simulating the concentration profiles of the system at CSS. Major operating variables are optimized based on the CSS behaviour in order to design an operation strategy that satisfies given requirements.

Section 2 presents a description of the continuous biobutanol fermentation process with ex-situ adsorption recovery. In Section 3, a dynamic model of the system is introduced. Section 4 discusses the approach to simulation and optimization of the CSS. The results and discussion of the simulation study are reported in Section 5. Section 6 contains a summary and conclusion of the research.

2. PROCESS DESCRIPTION

The proposed continuous biobutanol fermentation with an ex-situ adsorption recovery system is operated in the following four steps (Fig. 2).

Step 1 is the initial fermentation stage before the cyclic operation begins. The batch fermentation occurs with no feed or other flows into the system (Fig. 2A). When the concentration of butanol in the bioreactor reaches a specific value (to be determined by considering the butanol toxicity and the adsorption efficiency), the periodic operation involving Steps 2~4 begins.

In Step 2, the broth from the bioreactor is moved to the adsorption column till the adsorption column is filled to its target volume (Fig. 2B). In doing this, the volume of the bioreactor is lowered significantly. To compensate for this and maintain the concentration of the substrate at a certain level, the feed into the bioreactor is started at a constant rate.

After filling the adsorption column, the broth is circulated between the bioreactor and the adsorption column at a constant circulation rate, and both the fermentation and the adsorption occur simultaneously in Step 3 (Fig. 2C). The circulation goes on until the concentration of butanol in the adsorption column reaches the value specified in Step 1. In the beginning phase of the circulation, the concentrations of butanol and other products in the bioreactor decrease rapidly due to the fresh adsorbent in the column. About a while, the concentration of the products begin rising gradually back up since the capacity of the adsorbent is exceeded.

In Step 4, if the volume of the bioreactor is less than the initial level in Step 1, it is restored to the initial level by using the broth from the adsorption column (Fig. 2D). After that, the saturated column is replaced by a new one.

We repeat the process from Step 2 to Sep 4 with the new adsorption column. The broth remaining in the saturated column is transferred to the harvest tank for further processing. The saturated adsorbents are regenerated with steam, and the steam containing the desorbed butanol is collected in the product tank after condensing by the heat exchanger. The regenerated column is reused in a future run. In this study, one cycle is defined as the operation from Step 2 to Step 4; Step 1 is only performed to start the operation.

The feed rate and the circulation rate are the main operational degrees of freedom in this system. The feed rate directly affects glucose concentration and therefore cell concentration in the broth. Increase of the circulation rate widens the range of butanol concentration level during the operation as it speeds up the adsorption. Though the feed concentration is also decision variable, an operation strategy is designed assuming a given concentration in this study because of highly negative correlation between feed concentration and feed rate.

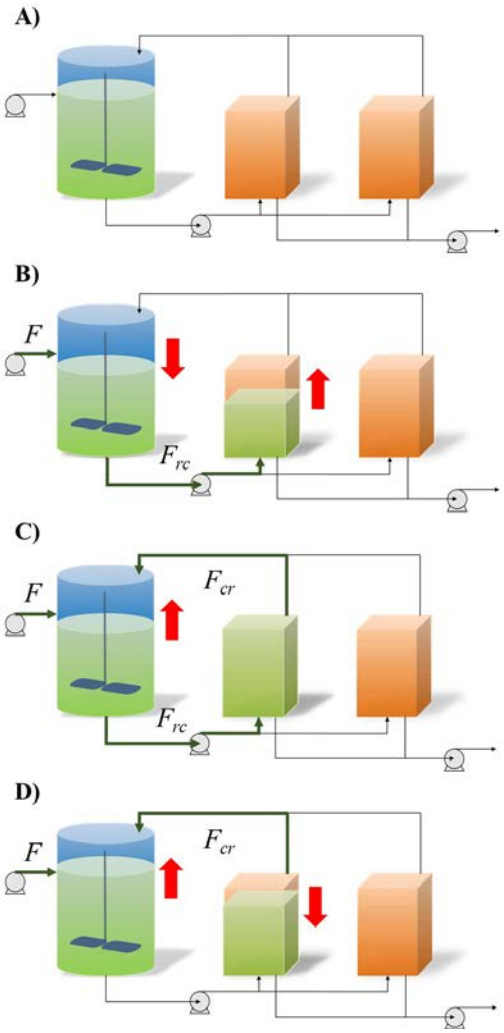

Fig. 2. Operation steps for the continuous biobutanol fermentation with ex-situ adsorption recovery A) Initial fermentation, B) Filling of the adsorption column, C) Circulation, D) Restoring the bioreactor volume.

3. DYNAMIC MODELING OF THE SYSTEM

The ABE fermentation occurs in the adsorption column as well as in the bioreactor, but the product adsorption occurs only in the adsorption column. Based on this, mass balance of each component such as cell, glucose, butanol and ethanol are constructed to describe dynamics of the system. In a previous study by the authors, a kinetic model for the adsorption column is developed by using the extended Langmuir theory (Eom et al., 2013); An ABE fermentation kinetic model is established mainly based on the Monod equation for cell growth and the Ludeking-Piert equation for product formation.

We assume that all concentrations in the bioreactor are spatially uniform (i.e., the contents are well-mixed), and changes in the volume by reactions and adsorption can be neglected. Though small amounts of other products such as acetone, acetic acid, and butyric acid are produced during the operation, they can be neglected for the purpose of this study. During fermentation, ethanol is maintained at a much lower concentration than its threshold of toxicity, and thus only butanol is considered as an inhibitor of cell growth.

Modified Monod equation used in this study indicates three inhibition effects on cell growth: substrate inhibition, product inhibition, and cell mass inhibition. The production rate is dependent on the cell concentration (Gaden, 1959), and combines the rates of growth associated and non-growth associated using the Ludeking-Piert equation (Luedeking and Piret, 1959). Also, the rate of substrate consumption has a similar form as the Luedeking-Piert equation. Detailed models and parameters of models are omitted due to space limitation. Please refer to a previous study (Kim et al., 2014).

The dynamic model of the system is built by connecting the dynamic model of bioreactor with that of the adsorption column. Eq. (1) ~ Eq. (3) shows the differential mass balances in the bioreactor, and they contain the effect of dilution and circulation. The variation in components' concentration caused by adsorption as well as circulation is considered to explain dynamics in the adsorption column (Eq. (4) ~ Eq. (6)).

$$\frac{dX_r}{dt} = \left(\mu_{net,r} - \frac{F}{V_r}\right) X_r + \left(X_{ad} - X_r\right)\frac{F_{cr}}{V_r} \tag{1}$$

$$\frac{dC_{r,S}}{dt} = \left(C_{f,S} - C_{r,S}\right)\frac{F}{V_r} + \frac{dS_r}{dt} + \left(C_{ad,S} - C_{r,S}\right)\frac{F_{cr}}{V_r} \tag{2}$$

$$\frac{dC_{r,j}}{dt} = \frac{dP_{r,j}}{dt} + \left(C_{ad,j} - C_{r,j}\right)\frac{F_{cr}}{V_r} - C_{r,j}\frac{F}{V_r}, \quad j = B, E \tag{3}$$

$$\frac{dX_{ad}}{dt} = \mu_{net,ad} X_{ad} + \left(X_r - X_{ad}\right)\frac{F_{rc}}{V_{ad}} \tag{4}$$

$$\frac{dC_{ad,S}}{dt} = \frac{dS_{ad}}{dt} + \left(C_{r,S} - C_{ad,S}\right)\frac{F_{rc}}{V_{ad}} \tag{5}$$

$$\frac{dC_{ad,j}}{dt} = \frac{dP_{ad,j}}{dt} + \left(C_{r,j} - C_{ad,j}\right)\frac{F_{rc}}{V_{ad}} - \frac{dA_j}{dt}, \quad j = B, E \tag{6}$$

where X_r and X_{ad} (g/L) is the concentrations of the cell mass in the bioreactor and the adsorption column, respectively. V_r is the volume of the bioreactor, and V_{ad} is the volume of the adsorption column (Fig. 1B). $C_{r,S}$, $C_{r,B}$ and $C_{r,E}$ are the concentrations of the substrate, butanol and ethanol in the bioreactor, respectively. F is the feed rate into the bioreactor, and $C_{f,s}$ is the substrate concentration in feed. dS_r/dt indicates the rate of substrate consumption in the bioreactor, and $dP_{r,j}/dt$ is variation in the concentration of butanol (j=B) and ethanol (j=E) in the bioreactor by product formation. Concentration with subscript ad means the same variable but in the adsorption column. dA_j/dt is the concentration change of component j by adsorption in the adsorption column. F_{rc} and F_{cr} are the circulation flow rate between the bioreactor and the adsorption column, and they are the same value during circulation (Step 3, Fig. 2C).

4. OPERATION OPTIMIZATION

In order to determine operation conditions leading to an optimal *Cyclic Steady State* (CSS) of the continuous biobutanol fermentation process, firstly, the CSS should be expressed as a function of the operating variables (i.e., degrees-of-freedom). The most straightforward way to determine the CSS condition called 'successive substitution' (Croft and LeVan, 1994) is adopted in this study. The optimization problem is defined in terms of process profit in Section 4.2; the optimization strategy is presented in Section 4.3.

4.1 Cyclic steady state (CSS)

When a system is forced periodically, its trajectory approaches a CSS, in which the system state at the end of a cycle returns exactly to the state at the beginning of the cycle (Croft and LeVan, 1994). Unlike the conventional steady state, in which the state variables are constant over time, the state variables at the CSS can vary with time during a cycle, thus complicating the determination. The CSS condition can be expressed by using the system model presented in Section 3, as follows:

$$\boldsymbol{x}_i(\mathrm{t_c}) = H(\boldsymbol{x}_i(0)) \tag{7}$$

$$\boldsymbol{x}_i(\mathrm{t_c}) = \boldsymbol{x}_i(0) \tag{8}$$

where $\boldsymbol{x}$ represents the vector of system states. H is the mapping (defined by the dynamic model) between the initial state $\boldsymbol{x}_i(0)$ and the end state $\boldsymbol{x}_i(\mathrm{t_c})$ of a cycle. i is the cycle index, and t_c is the time period of a cycle.

In simulating the model, the terminal state of a current cycle becomes the initial state of the next cycle, and this is repeated till the difference between every component of the initial states for two successive cycles becomes smaller than some tolerance (ε_{CSS}). In this study, the convergence is checked for the entire state trajectory of a cycle ($\forall t \in [0, t_c]$).

$$\left|\frac{x_i(\mathrm{t}) - x_{i+1}(\mathrm{t})}{x_i(\mathrm{t})}\right| \le \varepsilon_{CSS} \quad \forall t \in [0, t_c] \tag{9}$$

4.2 Optimization problem

The objective function of the optimization should include terms like butanol productivity and glucose loss. The latter term refers to the glucose contained in the broth discharged from the saturated adsorption column at the end of a cycle. Based on this, the objective function (J) to be maximized is chosen to take the following form:

$$J = w_1\left(\frac{q_B(t_c)\times m}{t_c} + \frac{C_{ad,B}(t_c)\times V_{ad}(t_c)}{t_c}\right) - w_2\left(\frac{C_{ad,S}(t_c)\times V_{ad}(t_c)}{t_c}\right) \quad (10)$$

The profit expression (under the CSS condition) is derived from subtracting the glucose loss per hour from the butanol productivity per hour. The butanol productivity over one cycle consists of the adsorbed butanol to the adsorbents and the remaining butanol which is not adsorbed in the adsorption column at switching time. The amount of adsorbed butanol is calculated by multiplying the amount of adsorbed butanol per unit mass of adsorbent q_B per cycle by the mass of adsorbent m. The quantity of remianing butanol in the discharged broth is expressed as the butanol concentration in the adsorption column $C_{ad,B}$ mutiplied by the liquid volumn of the column V_{ad} at the switching time. Loss of glucose can be obtained from the amount of remaining glucose in the discharged broth in a similar way to the quantity of remianing butanol in the discharged broth. Therefore, in order to maximize the profit, we have to maximize the butanol productivity and minimize the glucose loss with optimal optimization variables at CSS condition.

After one cycle, the broth in the saturated adsorption column is moved to a harvest tank and further fermentation occurs using the remaining glucose in the discharged broth. Although the remaining glucose is finally converted into products in a harvest tank, it brings a loss to the profit due to the delay in production. w_1 and w_2 are the weighting coefficients and the sum of them equals one. Since the glucose conversion yield coefficient is 0.35 for the ABE fementation, w_1 and w_2 are chosen to have the following values:

$$w_1 : w_2 = 1 : 0.35 = 0.74 : 0.26$$

There are several reqiuirements on the components of the bioreactor and the adsorption column, which are translated as the following inequality constraints:

$$0 \le C_{r,S}(\text{g/ L}) \le 9 \quad (11)$$

$$0 \le C_{r,E}(\text{g/ L}) \le 5 \quad (12)$$

$$\left(C_{r,B} - C_{ad,B}\right) / C_{r,B} \le 0.1 \quad (13)$$

Based on insights and experiences, Eq. (11) and Eq. (12) are the maximal allowable concentrations of glucose $C_{r,S}$ (g/L), and ethanol $C_{r,E}$ (g/L) in the bioreactor, respectively. In addition, the difference in the butanol concentrations of the bioreactor ($C_{r,B}$) and the adsorption column ($C_{ad,B}$) is required to be smaller than ten percent of $C_{r,B}$. Note that $C_{r,B}$ is larger than $C_{ad,B}$ owing to the adsorption occurring in the column. If the difference is higher than ten percent of $C_{r,B}$, the product recovery cost can be too high because of the low butanol concentration in the discharged broth.

The optimization problem with the nonlinear system model at the CSS can be stated as follows:

$$\begin{aligned} &\text{Max} \quad J(x,u,q) \\ &\text{s.t.} \quad F(\dot{x},x,u,q,t) = 0 \\ &\qquad D(x) \le 0 \\ &\left|\frac{x_i(\text{t}) - x_{i+1}(\text{t})}{x_i(\text{t})}\right| \le \varepsilon_{CSS} \quad \forall t \in [0, t_c] \\ &\qquad u_l \le u \le u_u \end{aligned} \quad (14)$$

Here J is the objective function (Eq. 10). Optimization variables u include the feed rate and the circulation rate, and F is the system model. D should be chosen such that inequalities represent the constraints specified earlier. u_l and u_u are the lower and the upper bounds on the optimization variables, respectively. Other design variables (represented by q) are fixed *a priori* (and therefore treated as constant parameters) based on insights and experiences gained during the laboratory and pilot experiments. For instance, the volume of the bioreactor is set as 200L, and the volume of the adsorption column without the absorbent is chosen to be one tenth of the bioreactor volume.

4.3 Optimization method

In the optimization, it should be first confirmed that the system has indeed reached *Cyclic Steady State* (CSS) with the tried input variables before evaluating objective function. Thus, dynamic simulation is a part of the optimization algorithm. The continuous biobutanol fermentation system exhibits highly nonlinear behavior at the CSS condition due to the terms describing the extended Langmuir isotherm and fermentation kinetics. In addition, the objective function and one of the constraints are nonlinear. The optimization problem is highly non-convex with a large number of local optima, making it difficult to find the global optimum.

Fortunately, the current problem has only two optimization variables with physical bounds and is amenable to an exhaustive search. First, the search domain of the two optimization variables is identified for a given feed concentration, and then the global optimum is found through a uniform grid search which is the simplest and most direct method to solve a bounded optimization problem (Neumaier, 2004, Pintér, 1996).

In defining the search domain S, the range of feed rate is chosen as 3L/h ~ 10L/h. In addition, the search range of circulation rate is determined as 150L/h ~ 250L/h in consideration of the pump cost and other design constraints. The entire search domain so defined is examined by gridding it with the grid size of 0.1L/h for feed rate and 10L/h for circulation rate. Infeasible regions of the search space (e.g., those that do not lead to a CSS at all or a CSS violating the constraints) are discarded (Horst and Romeijn, 2002, Zabinsky, 2003), resulting in a reduced search domain of *S'*. See Fig. 3 for an illustration.

Based on the reduced search domain *S'*, a more elaborate grid search is performed with finer grid sizes of 0.01L/h for feed rate and 1L/h for circulation rate (Fig. 3). All the grid points

over *S'* are evaluated in terms of the objective function and constraints, and the point giving the maximum (*J*) value is identified. Since the number of grid points increases exponentially with search dimension, the grid search is practical only for searches in one or two dimensions (Neumaier, 2004, Strongin and Sergeyev, 2000).

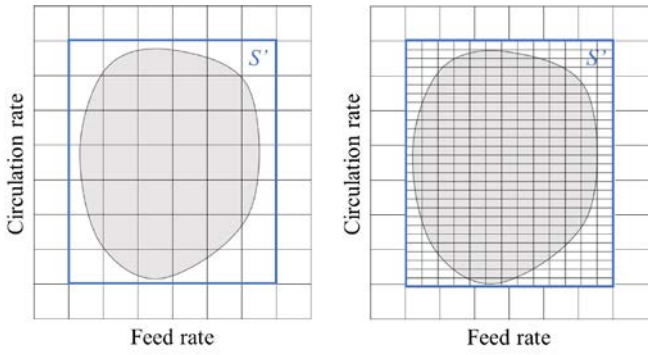

Fig. 3. Reduced search domain *S'* as a result of simple grid search (left), and discretized *S'* with finer size for an elaborate grid search (right).

5. RESULT AND DISCUSSION

Dynamic simulation is performed executing the step-wise sequence of process operation described in Section 2 *in silico* with the dynamic model presented in Section 3. In initializing the dynamic simulation and the associated nonlinear optimization, the concentrations of cell, butanol and ethanol (reported in Table 1) are set as the simulated values reached after 8 cycles. We set the initial concentration of glucose based on the design requirement. Given the unavoidable degradation in the adsorbent capacity, we assumed only 80% of the capacity of the adsorbent was available for the adsorption in simulation/optimization.

Table 1. Initial values for the simulation/optimization

Initial condition and inputs	Value (g/L)
Cell concentration	8.2508
Glucose concentration	10
Butanol concentration	7.2473
Ethanol concentration	0.3077

MATLAB's ordinary differential equation (ODE) solver of *ode15s*, recommended for a stiff system of equations, was used for the ODE integration. Fig. 4 shows the concentration profiles at the CSS resulting from the simulation, with the feed concentration of 250g/L, the feed rate of 6.44L/h, and the circulation rate of 245L/h; the relative tolerance parameter for the CSS condition was set as 10^{-3}. The simulated system attained the CSS after 43 cycles. With the constant rates of feed and circulation, the cell concentration is almost constant over the entire period at CSS, whereas the concentrations of butanol, ethanol and glucose follow more time-varying cyclic behavior (Fig. 4).

The concentrations of butanol and ethanol show cyclic behavior due to the periodic nature of adsorption and desorption, and this in turn causes a similar cyclic behavior in the glucose concentration. In the beginning phase of the CSS period, the amount of glucose consumed by the cells becomes larger as the butanol concentration is decreased by the rapid adsorption occurring in the adsorption column. After exceeding the capacity of the adsorbent, the glucose concentration creeps up because the rise in the butanol concentration leads to the inhibition effect, reducing the glucose consumption (Fig. 4).

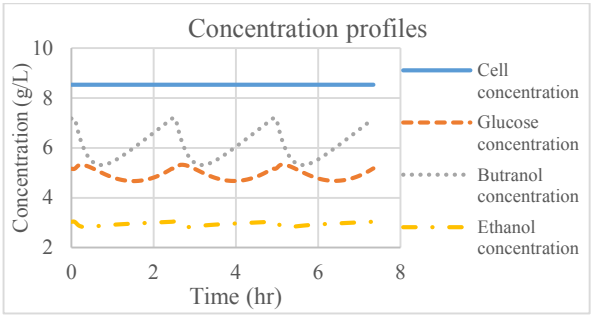

Fig. 4. The concentration profiles in a bioreactor at the CSS condition: the concentration of cell (line), glucose (dotted line), butanol (dashed line) and ethanol (dash-dotted line)

We carry out the optimization for several different feed concentrations with initial conditions presented in Table 1. Fig. 5 shows the optimal objective function values (with the previously given weighting factors) for four different feed concentrations: 200, 250, 300, and 350g/L. As expected, optimal feed rate increases as the feed concentration decreases. Note that, operation with a feed concentration lower than 200g/L leads to a bioreactor volume higher than its initial value at the switching time (violating the operation requirement) due to the large feed rate needed. A higher feed concentration gives a higher cell concentration than for a low feed concentration at CSS because a lower feed rate leads to a lower dilution rate. On the other hand, no significant correlation was seen between the optimal circulation rate and the feed concentration.

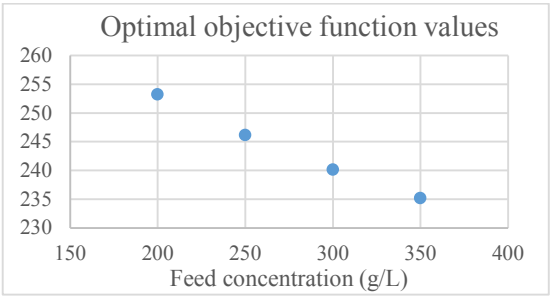

Fig. 5. The objective function values for different feed concentrations (with w1=0.74 and w2=0.26)

Table 2. The optimized operating variables

Feed concentration (g/L)	Feed rate (L/h)	Circulation rate (L/h)
200	7.64	250
250	6.22	249
300	5.23	250
350	4.5	250

To understand the effect of feed concentration on the objective function value, Fig. 6 plots the values of butanol productivity and glucose loss under the optimal CSS

condition for each of the tried feed concentration values. Since a reduction in the feed rate (corresponding to an increase in the feed concentration) leads to a larger restoration of the bioreactor volume by the broth circulated from the adsorption column, volume of the adsorption column at the switching time becomes smaller. According to Eq. (10), a decrease in the adsorption column volume at switching time $V_{ad}(t_c)$ reduces glucose loss but also causes a drop in butanol productivity. The decrease in butanol productivity dominates over the decrease in glucose loss (Fig. 6) and the objective function value becomes smaller as feed concentration increases.

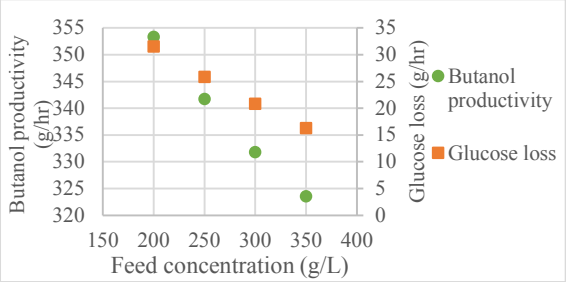

Fig. 6. The butanol productivity (circle) and the glucose loss (square) of each optimal operating condition for given feed concentration.

6. CONCLUSIONS

A bioreactor is integrated with an adsorption column to overcome the butanol inhibition effect on biobutanol production and to accomplish a continuous biobutanol production. The process exhibits cyclic concentration patterns due to the periodic switching of the adsorption column, and the highly nonlinear model combined nonlinear objective function and constraints leads to a highly non-convex optimization problem with a large number of local optima. This makes it difficult to find the global optimum. Since the problem has only two optimization variables with finite ranges set by physical considerations, optimal values for the feed rate and circulation rate can be decided for given feed concentration values through grid search to suggest an operation strategy. In the future, the optimization result should be evaluated on the pilot-scale plant, and the model and the operating strategy need to be improved. This will be followed by development of a control strategy based on sensitivity analysis and disturbance analysis.

This research was supported by the Advanced Biomass R&D Center (ABC) of the Global Frontier Project funded by the Ministry of Education, Science and Technology (ABC-2011-0031354) and by the R&D Center for Organic Wastes to Energy Business (under the Wastes to Energy Technology Development Program) funded by the Ministry of Environment, Republic of Korea (2013001580001).

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