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Optimum operating conditions in closed-system industrial acetifiers (semi-continuous operation): a study by computer simulation

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Abstract

This work analyzes the behaviour of an industrial acetification process in a closed system, by means of simulation techniques, testing several semi-continuous strategies, under different conditions of feed and discharge criteria. The simulator is based on a global model for the growth of *Acetobacter aceti* in submerged culture, which reflects the combined effects of acetic acid, ethanol and oxygen. The optimum operating conditions have been calculated for processes with both discharge at a set time and discharge at a set product concentration (acetic acid). In both cases, the effect on the evolution of the fermentation process by the ethanol and acetic acid concentration in the feed has been analyzed. © 1997 Elsevier Science S.A.

Keywords: Computer simulation; Industrial acetifiers; *Acetobacter aceti*

1. Introduction

Most industrial acetic acid fermentation processes designated as 'quick processes' operate by means of different production strategies based on multiple-chained batch fermentation steps. As a consequence, the global productivity of the industrial plants depends not only on the specific technology applied to the fermentative steps, but also on the operation strategy followed in the productive cycle. The first factor is normally related to gas–liquid mass transfer aspects, and the second factor is determined by task organization criteria. Therefore, studies of the optimization of production strategies are of considerable interest from an economical point of view at an industrial level.

Bearing in mind that the operation cycles of industrial acetic acid fermentation processes are usually long, experimentally searching for the optimum operation strategy involves very high economical costs. Moreover, because the characteristics of the different batch steps change very slowly from one step to the next, as a result of the homogenization effects, it is also very expensive to determine experimentally the features of the steady state in every one operation strategy, or to test if each strategy is stable or not.

In this sense, the use of optimization tools based on process simulators has been demonstrated to be of considerable interest for industrial fermentation processes. However, for the specific case of closed systems for acetic acid fermentation (with gas recirculation), there has not previously been a deep discussion in the literature about the optimum operation strategy to be applied. Thus, in this paper, we analyze the behaviour of an industrial acetification process (in a closed system), testing several semi-continuous strategies under different conditions of feed and discharge criteria. As a result of the factors mentioned above, we have used complex simulation techniques to develop this study.

2. The simulation tool

2.1. Kinetic model

The kinetic model used as the mathematical basis of the system, during the development of the simulator, has been discussed in depth in a previous paper [1]. It has also been successfully tested for the batch operation mode using an extensive data set, on both the industrial and laboratory scales. The fundamental equation of this model is based on the idea of biomass growth proposed by Sinclair and coworkers [2–

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4], which has been adequately developed in previous work [5,6].

Let X_v be the viable biomass concentration and let X_n be the non-viable biomass concentration. The substrates are ethanol (E, g l^{-1}) and oxygen (O, g l^{-1}), and the product is acetic acid (A, g l^{-1}). As the second equation of this model, a simplified scheme for substrate consumption and product formation is included [1], in which the consumption and formation rates are estimated solely as a function of the microorganism growth rate. We have

$$nX_v \xleftarrow{\mu_g} X_v \xrightarrow{\mu_d} X_n \qquad (1)$$

$$\mu_g=\frac{1}{X_v}\left(\frac{dX}{dt}\right),\quad \mu=\frac{1}{X_v}\left(\frac{dX_v}{dt}\right),\quad \mu_d=\frac{1}{X_v}\left(\frac{dX_n}{dt}\right) \qquad (2)$$

$$\mu=\mu_g-\mu_d \qquad (3)$$

$$\mu_g=\mu_m\left[\frac{E}{E+K_{SE}+(E/K_{IE})^2}\right]\left[\frac{1+(A/K_{SA})}{1+(A/K_{IA})^3}\right]\left[\frac{(O/K_{SO})}{1+(O/K_{IO})^3}\right] \qquad (4)$$

$$\mu_d=\frac{K_M A^4}{E^3+K_N} \qquad (5)$$

$$\left(-\frac{dE}{dt}\right)=\frac{\left(\frac{dX}{dt}\right)}{Y_{X/E}},\quad \left(\frac{dA}{dt}\right)=\frac{\left(-\frac{dE}{dt}\right)}{Y_{E/A}} \qquad (6)$$

For constant K_La processes, we have

$$\left(\frac{dO}{dt}\right)=K_La(O^*-O)-\frac{\left(\frac{dX}{dt}\right)}{Y_{X/O}} \qquad (7)$$

For constant dissolved oxygen processes, we have

$$O=cte \qquad (8)$$

The principal features of this kinetic model are as follows.

1. The consumption of ethanol and oxygen for the synthesis of cellular material, as well as for the maintenance of the cells, is negligible in comparison with the total consumption of substrate by the energetic route [7,8].
2. The formation of ethyl acetate by chemical means has no appreciable effect on the consumption of ethanol during the process, and also does not affect the total acetic acid produced [9].
3. The losses of ethanol by evaporation have not been considered in this model. The experiments used to fit the parameters were performed in a closed system which eliminates any possible loss of volatile compounds by evaporation.
4. The yield factors and stoichiometric coefficients are taken as being constant throughout the entire fermentation process.
5. The model is applied to isothermal processes. The coefficients and parameters used in the model were obtained at a temperature of 28 °C.

2.2. Simulation algorithms

The virtual semi-continuous fermenter used in this work exhibits the following main characteristics—most of the items are identical to those listed in the case of the batch operation mode [1].

1. The fermenter operates under well-controlled isothermal conditions at a temperature of 28 °C.
2. There is an automatic control system for the level of oxygen in the fermentation medium and the set point is fixed at 1.5 ppm (the value which should be maintained so that the growth of the micro-organism is within the optimum range) [1,10].
3. It is assumed that the loading rate and the discharge rate are very high in comparison with the fermentation rate or the mass transfer rate. In this case, any modification of the concentration during these operations, as a result of the fermentation process or the oxygen transfer phenomena, are irrelevant. Therefore, no length of theoretical time is provided for the operations of discharging and recharging to be carried out in comparison with the complete theoretical operation time.
4. The fermenter is considered to be full at the start of the fermentation process and to maintain a constant working volume during the entire course of the process (which also implies assuming that the discharging and recharging operations are instantaneous).
5. The recharging process takes place after the discharge and with identical volumes.
6. No account is taken of the possible effect that the modification of the specific medium conditions might have on the micro-organism viability equations.
7. Discharging is performed under two possible alternative criteria: (a) at set intervals of time (t_c); b) when the system reaches a given value of the acetic acid concentration (A_c).
8. The method of numerical integration used was the Runge–Kutta fourth-order type of route, using step widths of $\delta t=0.1$ h for all the simulations [11,12].
9. The flow diagram of the computer program that forms the basis of the simulator is shown in Fig. 1.

2.3. Kinetic model validation

As a result of the possible differences between the behaviour of biomass in the batch operation mode and in the semi-continuous operation mode, we have tested the simulation results of the kinetic model using several experimental data sets at different scales, in order to confirm the proposed values of the kinetic parameters.

The experimental data were obtained from two stirred cylindrical tanks, with respective volumes of 5 l and 250 l. The fermenter was equipped with a gas recirculation system and a dissolved oxygen control system, which enabled the set point to be easily maintained (± 10%). This system consisted of an oxygen electrode and a PID controller which, by

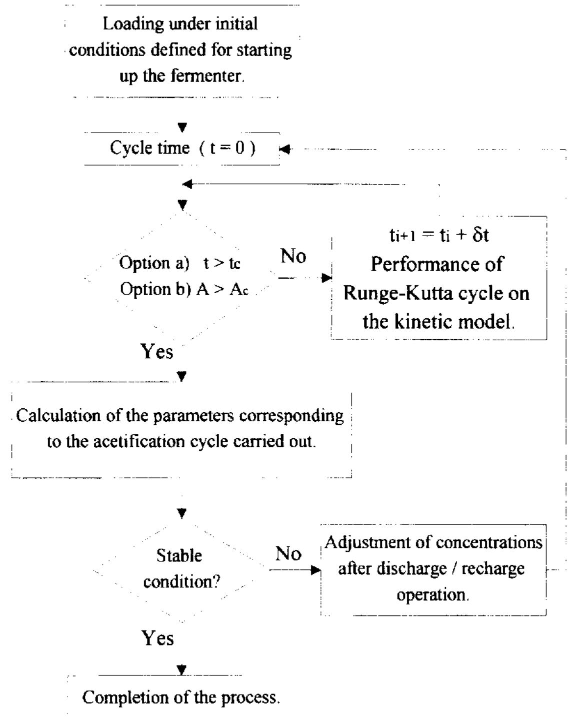


Fig. 1. Flow chart of simulation program developed for this study: (a) loading at set intervals of time (t_c); (b) loading at given acetic acid concentrations (A_c).

Table 1
Re-estimated values for the parameters of the proposed kinetic model for the semi-continuous operation mode

$\mu_m = 0.24\ h^{-1}$	$K_{IA} = 29.0\ g\ l^{-1}$
$K_{SE} = 19.6\ g\ l^{-1}$	$K_M = 0.101\ g^{-1}\ h^{-1}$
$K_{IE} = 3.03\ g\ l^{-1}$	$K_N = 2.5 \times 10^7\ g^3\ l^{-3}$
$K_{SA} = 11.7\ g\ l^{-1}$	$Y_{X/E} = 8.6 \times 10^{-3}$
$K_{SO} = 0.35$ ppm	$Y_{E/A} = 0.77$
$K_{IO} = 2.1$ ppm	$Y_{X/O} = 1.25 \times 10^{-2}$

actuating an solenoid valve, allowed the recirculation gas to be enriched to the extent consumed.

The fermentation medium used was a young wine of the Jerez winemaking area, with the following characteristics: ethanol, 70–80 g l^{-1}; total acidity tartaric acid, 0.5–1.0 g l^{-1}; sugar, 1–2 g l^{-1}; volatile esters, 1–5 mg l^{-1}; pH of between 2.9 and 3.1.

The micro-organism inoculated in all cases was a culture of *Acetobacter aceti*, as used industrially in the production of vinegar in the area, which is preserved in our departmental collection and classified as *Acetobacter aceti* UCA1. We carried out two different series of experimental fermentation cycles with multiple charges and different series of experimental fermentation cycles with multiple charges and discharges. The first series was carried out in 5 l tanks with oxygen control (constant dissolved oxygen) and the second series was carried out in 250 l tanks with K_La at constant levels (variable dissolved oxygen). Data corresponding to the latent phases were ignored, because this phase is difficult to evaluate, and it is not included in the model under study.

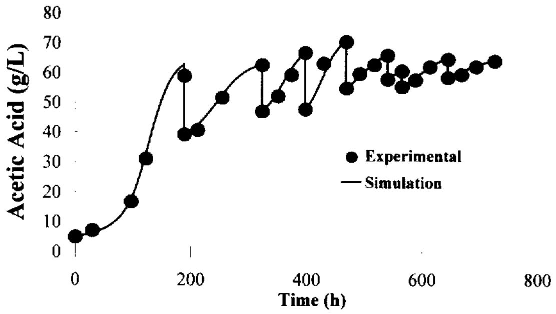


Fig. 2. Fit between an actual fermentation process and the simulation carried out, using semi-continuous operation mode with multiple discharge–recharge cycles.

The parameters of the model were re-estimated using non-linear least-squares analysis, which minimizes the differences between the experimental values of the adjustment variables and those obtained by simulation under the same conditions. As an adjustment variable, we have been using the acetic acid concentration in the discharging operation. After multiple iterations, the values of the kinetic parameter remained within the confidence range proposed in the original work for the discontinuous operation mode (batch fermentation). A modification of ±0.5% in each parameter produces errors of approximately ±5% in the value of the adjustment variables (Table 1).

An example of the agreement achieved between actual fermentation processes and simulated data is presented in Fig. 2.

2.4. Initial conditions and feed characteristics

As an overall point of departure in the simulation work, the initial conditions of the simulations were fixed according to an industrial fermentation process in which the inoculation phase has already taken place (ethanol, 70 g l^{-1}; acetic acid, 2 g l^{-1}; oxygen, 2 ppm; viable biomass, 8×10^6 cells per millilitre).

In relation to the feed parameters, it can be noted that feedstock in industrial acetifiers can be of very varied origins. This means that the ethanol concentration can vary from 6° to 12°GL (Gay-Lussac degree) or more. In contrast, the concentrations of acetic acid can vary within a much narrower range, or can even be zero in the case of wine which has not deteriorated biologically or partially fermented. Therefore, to standardize the simulation, the concentrations of the feedstock were fixed at 80 g l^{-1} for ethanol, 0.5 g l^{-1} for acetic acid and 6 ppm of dissolved oxygen.

3. Simulation runs

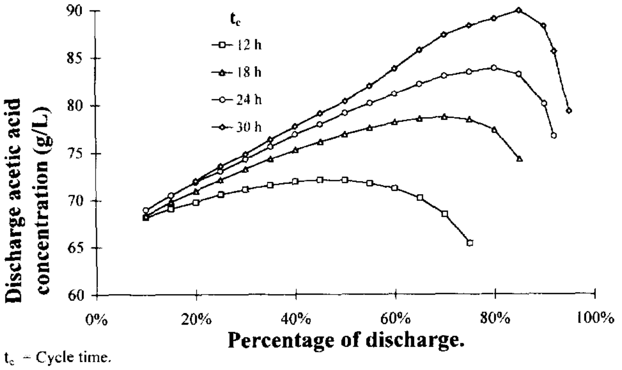
3.1. Discharging–recharging at set intervals of time

The simulations performed were aimed at obtaining the optimum discharging volume for different intervals of time between each loading. With intervals of 24 h (the typical interval in industrial-scale processes), we then carried out the analysis of the effect on the yields produced by different ethanol and acetic acid concentrations in the feed.

3.1.1. *Effect of the interval of time between each loading*

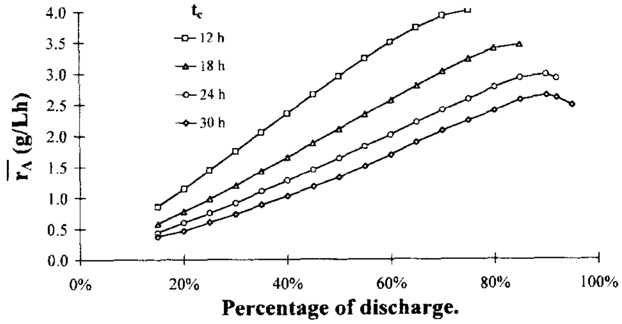
It should first be noted that, when operating at intervals of more than 30 h between each loading, the processes obtained are alternating, not homogeneous; in other words, a cycle with a high acetification rate and a high degree of final acidity is followed by a cycle of biomass recuperation, with low levels of acidity and slow acetification rates. The results obtained for cycles of less than 30 h are shown in Figs. 3 and 4. These figures give data for the final acetic acid and average acetification rate in a cycle, once the stable phase of the process has been reached. This stable phase is understood as being the condition when four consecutive cycles show evolution in the concentrations that differs by less than 0.5%.

On this basis, the acetification rates show clear increases for all the cycle times, in proportion with the increases in the volume loaded. This increase is continuous up to the level at which biomass washing in the fermenter is reached. This washing load is different for each cycle time, ranging from 75% for cycles of 12 h up to almost 95% for cycles of 30 h. However, it can be observed that the cycle times have very little effect on the results obtained when the percentages of discharge are small.



t_c – Cycle time.

Fig. 3. Simulation of semi-continuous fermentation processes with loading at fixed intervals of time, showing the acetic acid concentration in the output, after reaching a stable condition, for different time intervals and volumes of load.



$\bar{r}_A$ = Average acetification rate in a stable cycle.
t_c = Cycle time.

Fig. 4. Simulation of semi-continuous fermentation processes with loading at fixed intervals of time, showing the average acetification rate per cycle, after reaching a stable condition, for different time intervals and volumes of load.

The highest acetification rates are achieved with short cycles and high percentages of volume loaded; however, in contrast, low values of acidity are obtained in the discharge. As the length of the cycles increases, a clear decrease can be seen in the acetification rates, together with a significant increase in the degree of final acidity.

Based on the considerations noted above, the operating optimum will depend on the production requirements in terms of the degree of acidity.

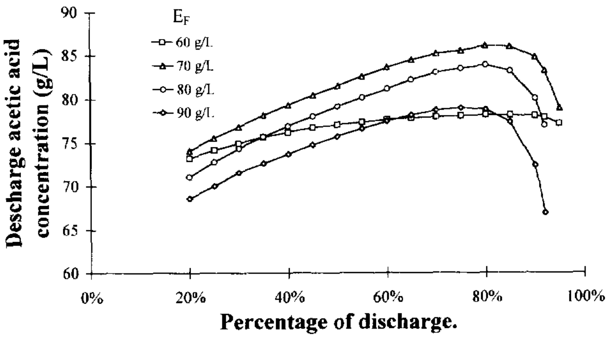
It should be noted that the percentages of discharge for maximum acidity and acetification rate increase in line with increases in the length of cycle time. This must be related to the degree of biomass dilution in each cycle, which is greater when the percentage of volume discharged is greater or when the cycle time is shorter. With a higher degree of dilution, a longer time will be needed for biomass growth.

3.1.2. *Effect of the ethanol concentration in the feed*

The process with cycles of 24 h (which is the cycle length most commonly used in the industry) was selected for the analysis of the effect of the ethanol concentration in the feed. The simulations were performed with ethanol concentrations increasing from 60 to 90 g l^{-1}, analyzing the results when a stable condition had been reached. In all the simulations analyzed, the initial concentrations were as previously described.

The average acetification rate did not undergo significant modification with the ethanol content, although a slight maximum could be discerned at an ethanol concentration of 75 g l^{-1}. However, the final acetic acid concentrations (Fig. 5) showed more irregular behaviour. A feed of 60 g l^{-1} yielded practically constant acetic acid values for whatever percentage of volume loaded. The reason for this is that, at this ethanol concentration, the conversion is total for all percentages of load.

In contrast, the same values of acidity are obtained with a feed of 70 g l^{-1} as with 60 g l^{-1}, for low percentages of volume discharged. However, the acidity increases as the



E_F = Ethanol concentration in the feed.

Fig. 5. Simulation of semi-continuous fermentation processes with loading at time intervals of 24 h, showing the acetic acid concentration in the output, after reaching stable condition, for different ethanol concentrations in the feed and volumes of load.

volume discharged increases, up to a maximum of around 90% in the case of feed at 70 g l^{-1}.

For a feed of higher concentration, the degree of final acidity is less than that for 70 g l^{-1}, which indicates that the lower yield of the process obtained in this conditions results from the greater inhibitory effect of the ethanol over the biomass.

On the basis of the simulations developed for this study, it can be proposed that the optimum operating level for semi-continuous processes of 24 h cycles consists of a discharge volume of 85%, with an ethanol concentration in the feed of 75 g l^{-1}. It can also be inferred from Fig. 5 that, when the feed contains a higher degree of alcohol, the discharge percentage for maximum acidity diminishes.

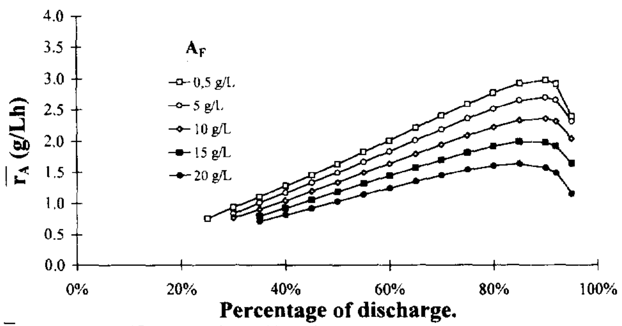
3.1.3. *Effect of the acetic acid concentration in the feed*

To analyze the effect of the acetic acid concentration in the feed, five different simulations have been performed with concentrations of this acid increasing from 0.5 to 20 g l^{-1}. The strong inhibitory effect of the acetic acid is clearly demonstrated in these simulations. Once a stable condition has been reached, the yields, the acetification rates and the degree of final acidity achieved all decrease as the degree of acidity in the feed increases. In Fig. 6, it can be observed that the acetification rates almost double as the acetic acid content of the feed is reduced from 20 to 0.5 g l^{-1}.

It can also be noted that modifying the degree of acidity of the feed does not appreciably affect the discharge percentage at which the highest values for acetification rates are achieved.

3.2. *Discharging–recharging at given value of acetic acid concentration*

This group of simulations was aimed at determining the optimum levels of operation when the system is recharged with a fixed concentration of acetic acid in the fermentation medium. With an acidity level set at 80 g l^{-1}, the effect of the ethanol and acetic acid concentrations in the feedstock on the fermentation yields was then analyzed.



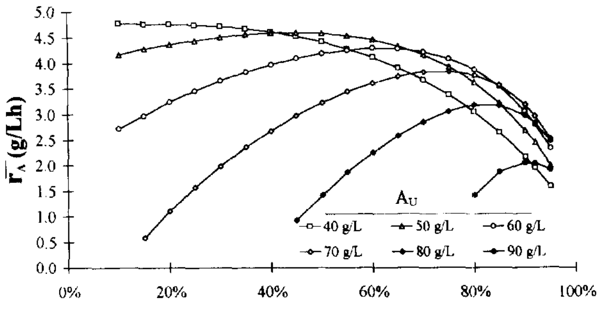
$\bar{r}_A$ = Average acetification rate in a stable cycle.
A_F = Acetic acid concentration in the feed.

Fig. 6. Simulation of semi-continuous fermentation processes with loading at time intervals of 24 h, showing the average acetification rate per cycle, after reaching a stable condition, for different acetic acid concentrations in the feed and volumes of load.

3.2.1. *Effect of the acetic acid content at the discharge*

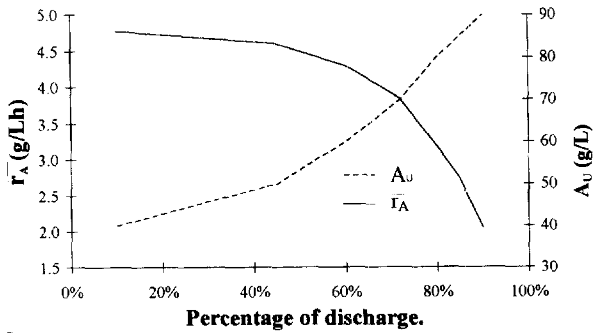
As can be seen in Fig. 7, the average acetification rates after reaching stability undergo an initial increase in line with the percentage loaded, before passing through a maximum and finally decreasing rapidly to almost zero (wash dilution time). The maximum acetification rate occurs at higher load percentage values the higher the acetic acid concentration is in the load. It can also be appreciated that the need to produce high values for the final acetic acid concentration compels a certain minimum value for the load percentage, because inhibition by the product acts as a brake on the process, which may then not reach a stable condition.

Fig. 8 shows a representation in a single graph of the three factors involved in the optimum working conditions considered: (1) the average acetification rate per cycle, which sets the overall rate for the process; (2) the final acetic acid concentration, which characterizes the quality of the production; (3) the volume percentage discharged in each cycle, which determines the operating conditions. Therefore, from this figure, the optimum value for the discharge volume to permit a higher acetification rate (4 g l^{-1} h^{-1}), combined with a higher acetic acid concentration in the output (79 g l^{-1}), can be estimated to be about 75%.



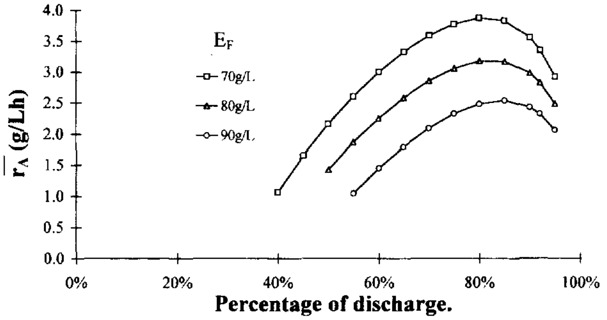
$\bar{r}_A$ = Average acetification rate in a stable cycle.
A_U = Acetic acid concentration in the dicharge.

Fig. 7. Simulation of semi-continuous fermentation processes with loading in cycles at fixed acidity levels, showing the average acetification rate per cycle, after reaching a stable condition, for different acetic acid concentrations in the feed and volumes of load.



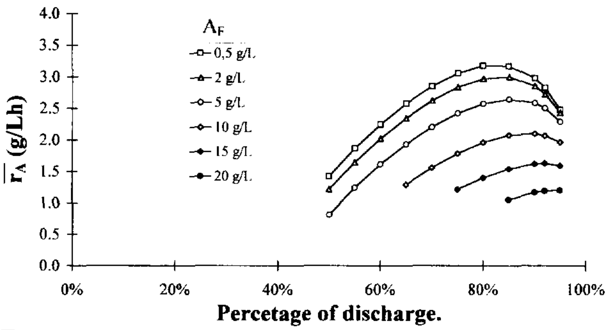
$\bar{r}_A$ = Average acetification rate in a stable cycle.
A_U = Acetic acid concentration in the dicharge.

Fig. 8. Simulation of semi-continuous fermentation processes with loading in cycles at fixed acidity levels, showing optimum operating levels.



$\bar{r}_A$ = Average acetification rate in a stable cycle.
E_F = Ethanol concentration in the feed.

Fig. 9. Simulation of semi-continuous fermentation processes with loading in cycles at a fixed acidity level of 80 g l^{-1}, showing the average acetification rate per cycle, after reaching stability, for different ethanol concentrations in the feed and volumes of load.



$\bar{r}_A$ = Average acetification rate in a stable cycle.
A_F = Acetic acid concentration in the feed.

Fig. 10. Simulation of semi-continuous fermentation processes with loading in cycles at a fixed acidity level of 80 g l^{-1}, showing the average acetification rate per cycle, after reaching a stable condition, for different acetic acid concentrations in the feed and volumes of load.

3.2.2. *Effect of the ethanol concentration in the feed*

The analysis of the effect of the ethanol concentration in the feed was undertaken by comparing the average acetification rates per cycle. Fig. 9 shows the results obtained for processes with ethanol feed concentrations of 70, 80 and 90 g l^{-1}; the criterion for the acetic acid concentration required on discharge was set at 80 g l^{-1}.

It can be seen that the higher the concentration of ethanol is in the feed, the higher is the load percentage needed for the fermenter to reach stability. A reduction in the average acetification rate per cycle, in proportion to the increase in the ethanol concentration of the feed, can also be observed.

3.2.3. *Effect of the acetic acid concentration in the feed*

Fig. 10 reflects the effect of the acetic acid concentration in the feed. As with the ethanol content, the values for the average acetification rate per cycle after reaching stability are shown against the percentages of volume discharged.

On comparing the different curves, it can be seen that the acetification rate reaches higher values when the acetic acid concentration in the feed is lower. It is also clear that lower percentages of load volume are required for the system to reach stability.

As a consequence, in a similar way to the other operation mode, the optimum working level under stable conditions is at the lowest possible acetic acid concentration in the feed and at percentages of volume discharged of around 80%.

4. Conclusions

On the basis of the these simulations, it can be concluded that the kinetic model used is reliable and versatile, because it gives coherent results that are consistent with the behaviour of industrial-scale acetic acid fermentation.

Under the working conditions used for the simulations, it can be stated that the optimum working levels for industrial acetic acid fermentation processes with discharge–recharge at fixed intervals of time follow clearly defined general rules.

1. The optimum period of time for each discharge–recharge is about 24 h—shorter intervals achieve higher acetification rates but with significantly lower acetic acid concentrations.
2. It is established that the best operating conditions require loading percentages of around 85%, with the following concentrations in the feedstock: about 75 g l^{-1} for ethanol and as low as possible for acetic acid.

Those semi-continuous fermentation processes with discharge–recharge undertaken when preset acetic acid concentrations are reached are ideal for producing vinegar of high acidity. The general rules that govern these processes are as follows.

1. The stronger the acetic acid concentration required in the discharge is, the greater is the percentage volume which must be discharged, if stability of operation is desired. However, this does involve a reduced average acetification rate in the cycle.
2. The feedstock should not exceed an ethanol content of 70 g l^{-1} and should have the lowest possible acetic acid content.

Appendix A. Nomenclature

A	acetic acid concentration (g l^{-1})
E	ethanol concentration (g l^{-1})
K_{Ij}	inhibition constant particular to species j (g l^{-1}, ppm)
K_M	first kinetic parameter for death rate (l g^{-1} h^{-1})
K_N	second kinetic parameter for death rate (g^3 l^{-3})
K_{Sj}	saturation constant particular to species j (g l^{-1}, ppm)
O	dissolved oxygen concentration (ppm)
O^*	equilibrium oxygen concentration in the medium (ppm)
$\bar{r}_A$	average acetification rate in a stable cycle (g l^{-1} h^{-1})
t	time (h)
δt	step width in the numerical integration (h)

X_v	viable biomass concentration (g Dry Weight l^{-1})
X_n	non-viable biomass concentration (g Dry Weight l^{-1})
X	total biomass concentration (g Dry Weight l^{-1})
$Y_{E/A}$	ethanol/acetic acid stoichiometric coefficient
$Y_{X/E}$	biomass/ethanol yield factor (g Dry Weight (g ethanol)$^{-1}$)
$Y_{X/O}$	biomass/oxygen yield factor (g Dry Weight (g oxygen)$^{-1}$)
μ	observed specific growth rate (h^{-1})
μ_d	specific death rate (h^{-1})
μ_g	gross specific growth rate (h^{-1})
μ_m	maximum specific growth rate (h^{-1})

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