Mathematical Model for Liquid-Gas Equilibrium in Acetic Acid Fermentations

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Abstract: An experimental study was conducted to propose an adequate mathematical model for liquid-gas equilibrium in acetic acid fermentations. Three operation scales (laboratory, pilot plant, and industrial plant) were employed to obtain the sets of experimental data. The proposed model, based in the UNIFAC method for the estimation of activity coefficients of a solution consisting of several components, takes into account the effect of emperature. However, in the set of equations, it has been necessary to put in the degree of equilibrium (ϵ). This coefficient adequately reflects the physical conditions of fermentation equipment. The experimental and numerical results help to define the fundamental mechanisms for liquid-gas equilibrium in these systems and demonstrate the model validity in the three tested scales. It was also found that in an industrial setting, closed systems are those with lowest evaporation losses. © 1998 John Wiley & Sons, Inc. *Biotechnol Bioeng* **59**: 310–317, 1998.

Keywords: acetic acid fermentation; liquid-gas equilibrium; evaporation losses; mathematical model; open fermentation system; semiclosed fermentation system; closed fermentation system; laboratory scale; pilot plant scale; industrial plant scale

INTRODUCTION

Evaporation of volatile compounds during acetic fermentation processes is one of the main causes of reduced yields on an industrial scale (Hamer, 1965a,b). Batch operation of large capacity plants (10,000 – 200,000 L) is common in this type of process. In this situation, given the need for extensive aeration of the medium, a large quantity of air saturated with volatile components leaves the fermentor. In general terms, losses of ethanol due to evaporation in industrial fermentation can result in reductions of 10% to 30% overall compared with the stochiometric yield, depending on the working temperature (Caro et al., 1992).

Given the increasing importance of this process in the fermentation industry, an in-depth study of the liquid-gas equilibrium which is established between the liquid phase (the fermentation medium) and the gaseous phase (outflow from the fermentor) is of general interest; equally useful would be to derive a model of evaporation appropriate for the general processes of acetic fermentation on an industrial scale.

MATHEMATICAL MODEL

In general, it can be assumed that the phenomenon of evaporation during the industrial fermentation process is controlled exclusively by the thermodynamic equilibrium established between the bubbles of gas and the liquid phase. These bubbles of the gaseous phase are produced as a result of the aeration required in the fermentors to maintain adequate levels of oxygenation; the liquid phase is constituted by the fermentation medium itself. The approximation to the condition of thermodynamic equilibrium is reasonable taking into account that the size of the gas bubbles ranges between 1 and 3 mm diameter, and that only very small quantities of liquid are mechanically drawn off by the gas flow (Hamer, 1965a,b).

In the model proposed, it is assumed that the gaseous phase is comprised exclusively of the main volatile components of the fermentation medium and of air (oxygen, nitrogen, etc.), in other words, air (N), water (W), ethanol (E), and acetic acid (A). It is also assumed that the result of the partial pressures generated is simply additive. On these bases, the composition of the gas can be represented by the following system of equations:

$$P = P_N + P_W + P_E + P_A \tag{1}$$

$$Y_A = \frac{P_A}{P};\ Y_E = \frac{P_E}{P};\ Y_W = \frac{P_W}{P};\ Y_N = 1 - Y_A - Y_E - Y_W \tag{2}$$

where P is the total pressure of the gas in the gaseous flow (normally atmospheric pressure); P_i is the partial pressure of the component i for acetic acid (A), ethanol (E), water (W), or air (N); Y_i is the molar fraction of the compound i in the gaseous phase for acetic acid (A), ethanol (E), water (W), or air (N). P_N can be obtained as the sum of all the partial pressures of the components of the air.

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Because the liquid phase of fermentation is not an ideal system, it is necessary to apply the following equilibrium equation:

$$P_i = P_i^0 \gamma_i X_i \qquad (3)$$

where P_i^0 is the vapor pressure of the pure component i; γ_i is the activity coefficient of the component i; and X_i is the molar fraction of the component i in the liquid phase, which can be measured experimentally.

To calculate P_i^0, in accordance with the temperature of the medium, Antoine's equation of seven parameters can be used, among others (Walas, 1985):

$$Lnp_i^0 = ANT1 + \frac{ANT2}{ANT3 + T} + ANT4\ T + ANT5\ Ln(T) + ANT6\ T^{ANT\,7} \qquad (4)$$

where the constants $ANT1$ to $ANT7$ are the corresponding coefficients of Antoine's equation (Table I), which depend on the compound in question.

$$-\left(\frac{di}{dt}\right)_{EVAP} = \frac{Q\,MW_i}{MV} Y_i \qquad (5)$$

where the term $-(di/dt)_{EVAP}$ is expressed in g/L$_{\mathrm{medium}}$ h, Q is the flow rate of aeration expressed in L$_{\mathrm{air}}$/L$_{\mathrm{medium}}$ h, MW_i is the molecular weight of the substance i in g/mol, Y_i is the molar fraction of the substance i in the gas flow and MV is the molar volume of the gas outflow, expressed as L$_{\mathrm{air}}$/mol. In this expression, the approximation is made that the outflow from the fermentor is considered as pure air, because the volatile compounds of the fermentation medium represent a very low molar fraction compared with the total quantity of air given off. Additionally, the air is taken to be an ideal gas and the equation for perfect gases is applied to calculate its molar volume, as a function of the working temperature in each case:

$$MV = \frac{R\,T}{P} \qquad (6)$$

where R = 0.082 atm L/mol K; T(K) and P = 1 atm (working pressure).

Table I. Values of the parameters of Antoine's equation for ethanol, water, and acetic acid, between the temperature limits indicated (Walas, 1985). Homogeneous coefficients, with the pressure (Pascal) and the temperature (Kelvin).

Parameter	Ethanol	Water	Acetic acid
ANT1	–75,7609	–31,3974	–142,7170
ANT2	–3100,6470	–2046,370	0,2266
ANT3	–40,5006	–75,4022	–330,9145
ANT4	–0,0881	–0,0121	–0,0463
ANT5	20,8120	9,1657	28,8203
ANT6	$5{,}04510^{-4}$	$4{,}879\ 10^{-18}$	$1{,}377\ 10^{-11}$
ANT7	2,0	6,0	4,0
T_{min}(K)	206,4	273,2	295
T_{max}(K)	516,2	647,3	594,4

With regard to the coefficients of the liquid phase (Y_i), it is a reasonable first approximation to assign a value of 1 to Y_W, considering the high proportion of water in the liquid phase. In the cases of ethanol and acetic acid, however, their values must be accurately established, because this coefficient depends on the temperature, concentration, and other factors. In principle, the estimation of Y_E and Y_A can be simplified, ignoring the influence of the salts and other components dissolved in the medium. The procedure adopted in this model to calculate the value of the coefficients of activity of the compounds referred to, is based on the UNIFAC method of contribution of groups, whose theoretical basis is found in the calculation of the excess Gibbs energy (G^E) between the two phases, using the UNIQUAC equation (Walas, 1985; Klotz and Rosenberg, 1981; McDonald and Floudas, 1995):

$$\frac{G^E}{RT} = \sum_{i=1}^{n} X_i \operatorname{Ln}\gamma_i \qquad (7)$$

where n is the number of components in the mixture.

Essentially, the UNIQUAC equation (UNIversal QUAsi-Chemical equation) assumes that the excess Gibbs energy is determined by the conjunction of two independent effects: a first effect due to the differences in the size and form of the molecules (the configurational or combinatorial effect) and a second effect due to the energetic interactions between them (the residual effect).

UNIFAC Method (UNIquac Functional Group Activity Coefficients)

This is a method of calculation that gives a very close approximation of the value of the activity coefficients of a solution consisting of several components and has its theoretical basis in the UNIQUAC equation. According to this method, the effects which contribute to the values of the activity coefficients are considered to be of two types: ''configurational'' (C) and ''residual'' (R):

$$\operatorname{Ln}\gamma_i = \operatorname{Ln}\gamma_i^c + \operatorname{Ln}\gamma_i^R \qquad (8)$$

To find the values of these contributions, it is assumed that each molecule of the system is formed by a series of functional groups characterized by a group volume parameter (R_K) and a group surface parameter (Q_K); whereas the interactions between the different groups of which the molecules consist are reflected by the group interaction parameters (a_{kl} and a_{lk}).

In the case of the ethanol/water/acetic acid system, group volume and area coefficients of the constituent molecules are given in Table II, and the interaction parameters between the groups in Table III.

First, the configurational part is calculated according to the following expression:

$$\operatorname{Ln}\gamma_i^c = \operatorname{Ln}\frac{\phi_i}{X_i} + \frac{Z}{2} q_i \operatorname{Ln}\frac{\theta_i}{\phi_i} + \sum_j \phi_j\left(l_i - \frac{r_i}{r_j} l_j\right) \qquad (9)$$

Table II. Volume parameters (R_k) and area parameters (Q_k) corresponding to the groups comprising the ethanol/water/acetic acid system.

N^0	Group	R_k	Q_k
1	CH_3	0,9011	0,8480
2	CH_2	0,6744	0,5400
3	OH	1,0000	1,2000
4	COOH	1,3013	1,2240
5	H_2O	0,9200	1,4000

[a] Achard et al., 1994; Fredenslund et al., 1977; Gmehling and Ouken, 1979; Krummins et al., 1980; Reid et al., 1977; Skjold-Jorgensen et al., 1979; Zarkarian et al., 1979.

the subscript "j" being the remaining components of the solution different from "i," and "Z" being the number of coordination of the molecules in the mixture, which is given by the following expression:

$$Z = 35.2 - 0.1272\,T - 0.00014\,T^2 \qquad (10)$$

Volume contribution of each of the molecules comprising the solution (r_i) is calculated in the following way (Abrams and Prausnitz, 1975):

$$r_i = \sum_k v_k R_k \qquad (11)$$

where the subscript "i" corresponds to each molecule, and "k" refers to the groups which form the molecules; "v" represents the stoichiometry of each group in the corresponding molecule. Similarly, the surface contributions (q_i) will be given by (Abrams and Prausnitz, 1975):

$$q_i = \sum_l v_l Q_l \qquad (12)$$

Further, it is possible to define the volume fraction of each molecule as:

$$\phi_i = \frac{X_i r_i}{\sum_i X_i r_i} \qquad (13)$$

And, in an analogous way, the surface fraction corresponding to each of the substances comprising the solution is:

$$\theta_i = \frac{X_i q_i}{\sum_i X_i q_i} \qquad (14)$$

Table III. Interaction Parameters (a_{kl}) corresponding to the groups comprising the ethanol/water/acetic acid system.

a_{kl}	1	2	3	4	5
1	0	0	986,5	663,5	1318
2	0	0	986,5	663,5	1318
3	156,4	156,4	0	199,0	353,5
4	315,3	315,3	−151,0	0	−66,17
5	300	300	−229,1	−14,09	0

[a] Achard et al., 1994; Fredenslund et al., 1977; Gmehling and Ouken, 1979; Krummins et al., 1980; Reid et al., 1977; Skjold-Jorgensen et al., 1979; Zarkarian et al., 1979.

However, these volume and surface fractions are not enough to determine completely the configurational interaction of the system; for this, it is necessary to define the weighted surface-volume parameter. In this parameter (l_i), the previously determined fractions, as well as the number of coordination, are included:

$$l_i = \frac{Z}{2}(r_i - q_i) - (r_i - 1) \qquad (15)$$

When all these parameters have been defined, the calculation of the configurational part of the activity coefficients can be made.

Secondly, the equation giving the residual contribution of the activity coefficient is the following:

$$\mathrm{Ln}\,\gamma_i^R = \sum_k Q_k\,(\mathrm{Ln}\,\Gamma_k - \mathrm{Ln}^i\,\Gamma_k) \qquad (16)$$

The value given to magnitude Γ_k is for the mixture, while that for ${}^i\Gamma_k$ is the equivalent for the pure component "i":

$$\mathrm{Ln}\Gamma_k = Q_k\,(1 - \mathrm{Ln}E_k - F_k) \qquad (17)$$

Values are similarly given to the magnitudes E_k and F_k for both, the mixture and for the pure components in the following way:

$$E_k = \sum_l \theta_l \psi_{lk}\ ;\ F_k = \sum_i \frac{\theta_l \psi_{kl}}{E_l} \qquad (18,19)$$

Also, the surface fraction of the group "l" is defined by θ_l:

$$\theta_l = X_l \frac{Q_l}{\sum_k X_k Q_k} \qquad (20)$$

and the function of interaction ψ_{kl} as follows:

$$\psi_{kl} = exp\left(-\frac{a_{kl}}{T}\right) \qquad (21)$$

It only remains to define the fraction of the group "l" in the mixture (X_l) as:

$$X_l = \frac{1}{S}\sum_i v_{li} X_i \qquad (22)$$

and the fraction of the group "l" in the pure component "i" (${}^iX_l$), making $X_i = 1$ in the preceding equation, as:

$${}^iX_l = \frac{1}{S}\sum_i v_{li} \qquad (23)$$

where "S" in the case of the mixture has the value:

$$S = \sum_i (X_i \sum_k v_{ki}) \qquad (24)$$

and in the case of the pure component has the value:

$$S = \sum_i \sum_k \nu_{ki} \qquad (25)$$

In both cases, ν_{ki} represents the number of distinct atoms of H in the group "k" of the molecule of the component "i."

In this way, the residual part of the coefficients of activity for the system under study is also completely defined.

Consequently, by using the full set of equations (1) to (25) and the values of the parameters shown in Tables I, II, and III, a theoretical model is provided which will estimate the rate of evaporation of the volatile components in acetic fermentation processes, for a given aeration flow rate and a given composition of ethanol and acetic acid in the fermentative medium.

The flow diagram for the calculation program corresponding to the model is shown as Figure 1.

EXPERIMENTAL APPARATUS AND PROCEDURE

To study the processes of acetic fermentations from the point of view of the losses suffered through evaporation, various experiments were conducted at different temperatures fixed between 20°C and 30°C, which is the usual range for this type of fermentation on an industrial scale. All the experiments used a submerged culture of one of the microorganism strains most commonly employed in the industrial production of vinegar, classified taxonomically as *Acetobacter aceti* ATCC 15973.

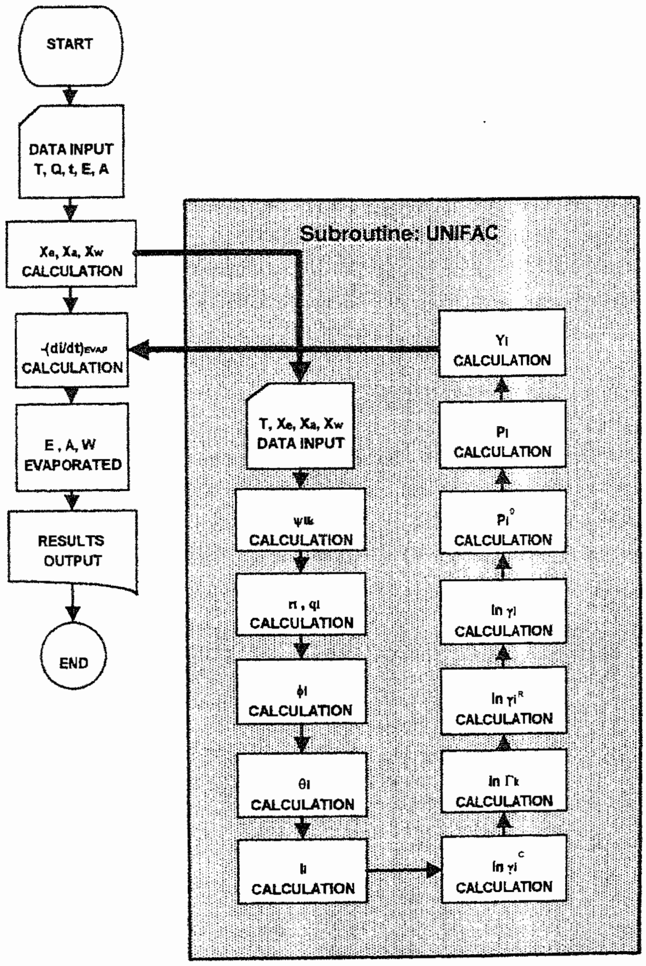

Figure 1. Flow diagram for the calculation program corresponding to the mathematical model.

The capacities of the three sets of equipment used were: 5 L, 1,000 L, and 10,000 L; aeration flow rates were between 0.0032 vvm and 0.2 vvm and the agitation rate was 400 rpm. The oxygen transfer coefficient from the gaseous phase to the liquid phase was determined by the absorption-desorption method; in all the systems used, this coefficient was above 100 h^{-1}, which assured the supply of oxygen necessary for the different conditions of operation studied.

The substrate used in all the experiments was a complex natural medium constituted by a young wine from the Jerez production area, with the following constituents: ethanol: 70 – 90 g/L; total acidity: 15 – 20 g of tartaric acid/L; sugars: 1 – 2 g/L; higher alcohols: 0.5 – 1.0 g/L; volatile esters: 1 – 5 mg/L; pH: 2.9 – 3.1; sulfur dioxide: 60 – 70 mg/L. This medium was sterilized for 20 min at 120°C, and the pH later fixed at 4 with KOH 1*M,* to ensure the most suitable conditions for microorganism growth.

Schematic diagrams of the three sets of equipment used in the experimentation are presented in Figures 2, 3, and 4. The simplest of the three is the open system (Fig. 2); this consists of an automatic, thermostatically controlled fermentor equipped with mechanical agitation and aeration completely open to the atmosphere, automatic control is by the PID computer system.

The semi-closed fermentation system (Fig. 3) is analogous to the first system but adapted by the addition of two columns of 5 cm ID and 100 cm height, with Raschig 1 cm rings as filling to a height of 70 cm. The gas outflow from the fermentor is passed through the first column (the absorption column) which contains water; this water is then

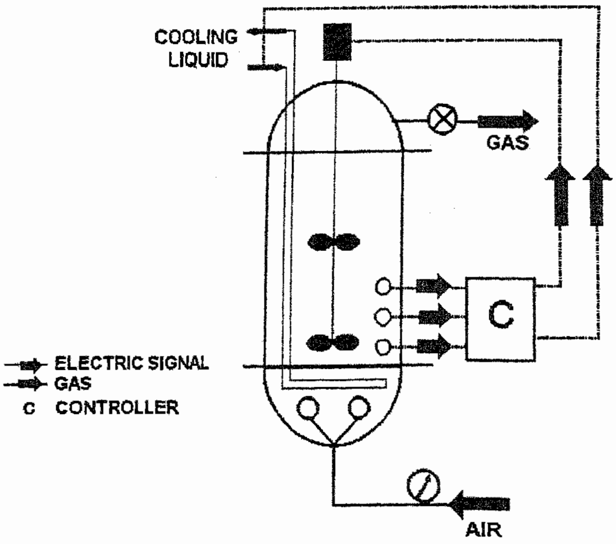

Figure 2. Open system schematic diagram.

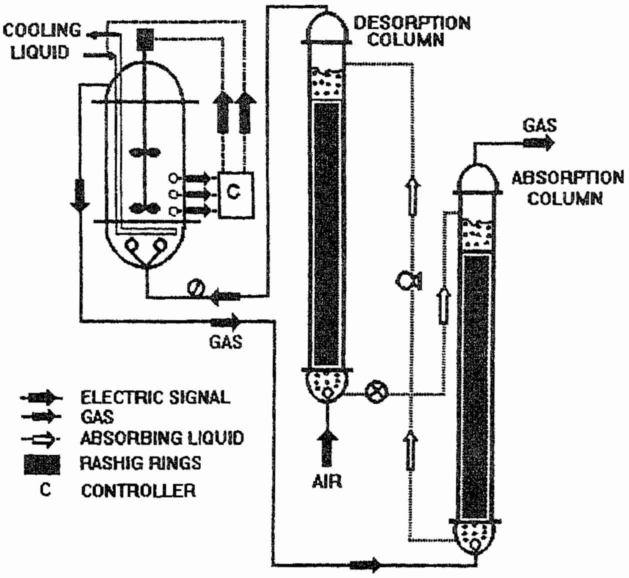

Figure 3. Semi-closed system schematic diagram.

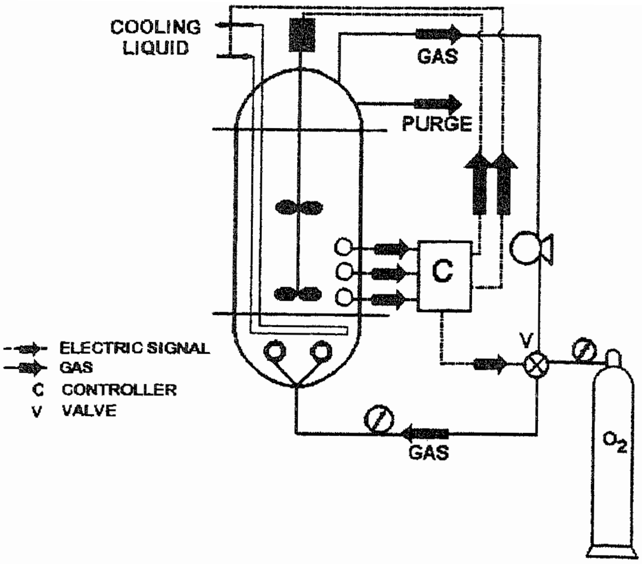

Figure 4. Closed system schematic diagram.

recirculated through the second column (the desorption column), through which flows the clean air before its introduction into the fermentor. Water recirculation is by a peristaltic pump and an electronic device controls the level of water in the columns.

The third type of fermentation equipment used (Fig. 4) is the closed system, consisting of a fermentor which operates under a closed gas circuit, preventing the escape of volatile compounds in the gas outflow. Discrete quantities of oxygen are injected into the recirculation gas flow to the fermentor, to compensate for the consumption by the biomass. The system is fitted with a dissolved oxygen electrode and a controller for the injections necessary to maintain dissolved oxygen at the required level, thus operating within a tolerance of ±10% of the set level.

In all the experiments, the inoculation of the fermentor was made by adding to the initial sterile medium, a volume equivalent to 10% of the total capacity, of previously prepared inoculum. This inoculum was comprised of a medium with analogous characteristics to that of the fermentation, showing a high rate of growth of *Acetobacter aceti;* preparation was by parallel acetic fermentation in incubation chambers. Before each inoculation, the stability of the operating variables and the correct operation of the control devices were checked.

The acetic fermentation experiments were monitored by taking samples at regular time intervals, and performing the following determinations: concentration of ethanol by gas chromatography (Sanz et al., 1987) and concentration of acetic acid by potentiometric measurement (Drysdale and Fleet, 1988); pH, concentration of dissolved oxygen, and temperature of the fermentation medium was continuously recorded by the appropriate equipment.

A summary of the operating conditions of the series of experiments conducted is shown in Table IV.

EXPERIMENTAL RESULTS

In all the experiments conducted, the true quantity of ethanol evaporated during each time interval was calculated from the quantity lost from the medium, but deducting the quantity assimilated by the microorganism during the fermentative process; this assimilated quantity is easily calcu-

Table IV. Summary of the experimentation conducted. The concentration ranges of ethanol and acetic acid indicated give the values at the beginning and end of the experiment.

Scale	No. of experiments	System	Temp. (°C)	Air (vvm)	Dissolved oxygen (ppm)	Ethanol(E_0-E_f) (g/L)	Acetic acid (A_o-A_f) (g/L)
Laboratory (5L)	3	Semi-closed	26°C	0.2	7	80–25	0,4–33
	3	Open	26°C	0.2	7	80–25	0,4–33
	3	Semi-closed	26°C	0.05	7	80–0	1,5–58
	3	Open	26°C	0.05	7	80–0	1,5–58
Pilot plant (1,000L)	2	Closed	28°C	0.2	7	47–22	40–74
	2	Open	30°C	0.032	7	48–15	40–70
Industrial plant (10,000L)	3	Open	20°C	0.0032	1	50–20	40–80
	3	Open	25°C	0.0032	1	50–20	40–80

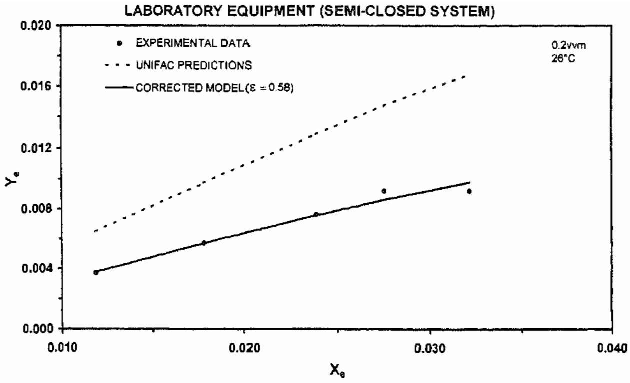

Figure 5. Experimental data, UNIFAC predictions and corrected model data for laboratory scale semiclosed system (0.2 vvm and 26°C).

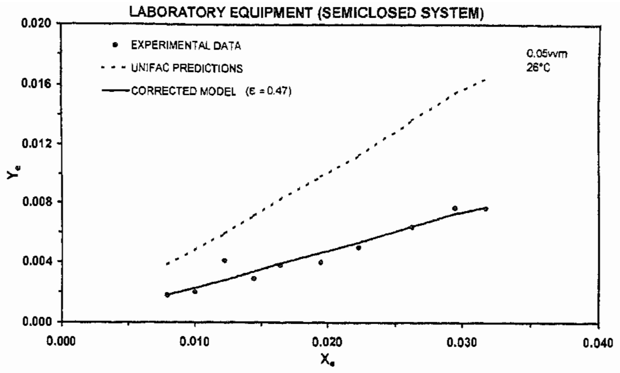

Figure 7. Experimental data, UNIFAC predictions and corrected model data for laboratory scale semi-closed system (0.05 vvm and 26°C).

lated from the stoichiometry of the fermentative process between the ethanol and the acetic acid (1:1) and by measuring the quantity of acetic acid produced during the time interval under study.

In fact, the quantities of acetic acid evaporated during the process are minimal in comparison with the quantity present in the liquid phase, but in the case of ethanol, the phenomenon of evaporation is of real economic significance. In this study, the evaporation of water and acetic acid have been considered negligible and the calculations have centered on the evaporation of ethanol.

It is possible to make comparisons between the true rates of evaporation and those calculated by the model; however, comparison of the data of the molar fractions in the gaseous phase, with those in the liquid phase, gives results more independent of the experimental conditions. The results expressed in this form are given in Figure 5 to 12.

As can be observed, the theoretical predictions of the model are, in most cases, higher than the experimental data. Probably, the hypothesis of equilibrium between the phases is less exact under the experimental conditions than in the model; the gas outflow from the fermentor may not be in equilibrium with the liquid phase. This effect may be the result of insufficient contact time between the two phases for the equilibrium conditions to be established, for this difference is more noticeable when the time spent by the bubbles moving through the medium in the reactor is shorter.

Accepting therefore, the existence of a variance with respect to the equilibrium, the degree of equilibrium (ε) is defined as the fraction of the theoretical equilibrium reached in each of the experiments. This is calculated as the average of the quotient between the molar fraction of ethanol in the vapor given by the evaporation model (theoretical Y_E) and the true molar fraction of ethanol in the gas (experimental Y_E). This calculation assumes that the theoretical predictions refer to the condition of equilibrium, which constitutes one of the original hypotheses underlying the UNIFAC calculation.

In the case of the systems employed in the experimentation, the degree of equilibrium (ε) depends fundamentally on the flow rate of aeration and on the height of the liquid phase in the reactor; so when the system is operated with high aeration flow rates, the rate at which the gas passes through the liquid phase is also high and therefore, the time of contact between the phases is less. In the same way, the higher the level of the medium in the fermentor, (generally commensurate with a larger volume of fermentation medium), for a given rate of aeration, the longer the contact time and the higher the degree of equilibrium reached.

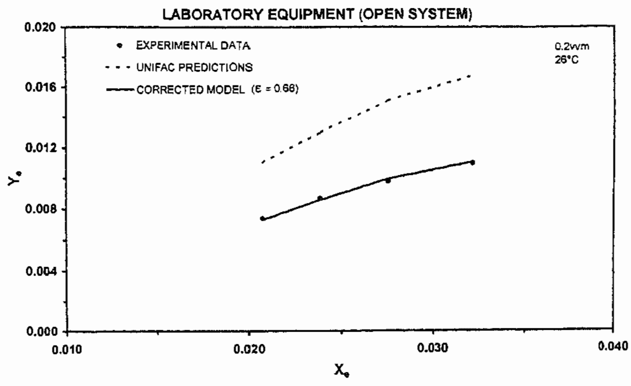

Figure 6. Experimental data, UNIFAC predictions and corrected model data for laboratory scale open system (0.2 vvm and 26°C).

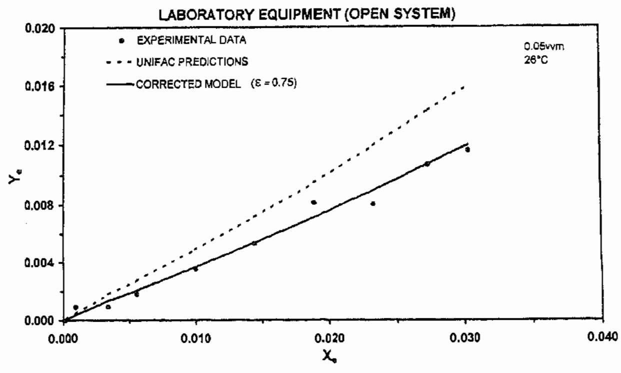

Figure 8. Experimental data, UNIFAC predictions and corrected model data for laboratory scale open system (0.05 vvm and 26°C).

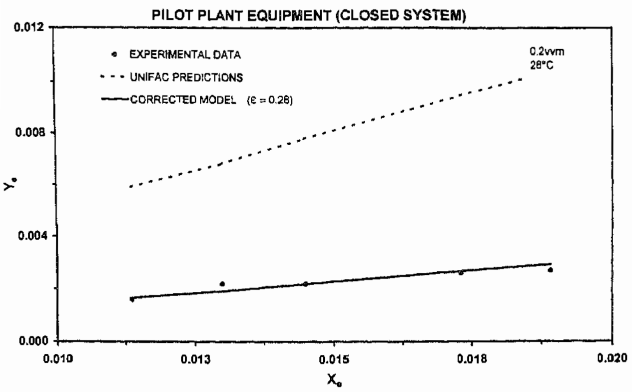

Figure 9. Experimental data, UNIFAC predictions and corrected model data for pilot plant scale closed system (0.2 vvm and 28°C).

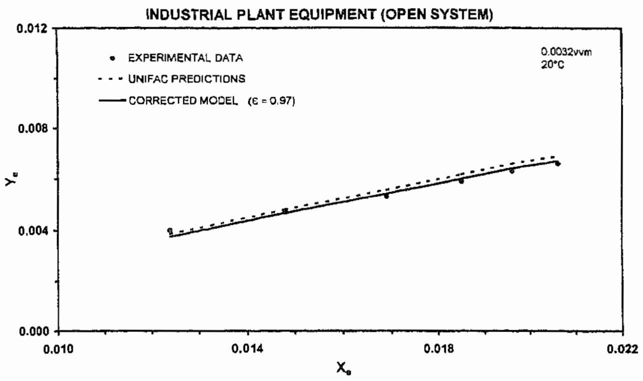

Figure 11. Experimental data, UNIFAC predictions and corrected model data for industrial plant scale open system (0.0032 vvm and 20°C).

In addition to the degree of equilibrium (ϵ), there may be other factors operating, to a less significant extent, to widen the gap between theoretical and experimental data. Among these factors should be mentioned the influence of the dissolved salts in the fermentation medium, also known as the ‘‘salting out effect’’ (Kikic and Fermeglia, 1991; Walas, 1985). However, these factors have not been included in this calculation of degree of equilibrium, because they are all negligible in the conditions of experimentation, compared with the previously-described effect.

In Table V are given the values of (ϵ) calculated for all the systems and scales of operation tested, together with the correlation obtained between the experimental and theoretical (R^2) data, the value of (ϵ) obtained being considered a valid factor of modification. The degrees of equilibrium reached show values ranging from 0.28 to 1.

As a general observation, it can be seen that the degree of equilibrium is less in semi-closed or closed systems, basically because the working volume is small and the average passage of the bubbles of gas through the medium is short; this leads to molar fractions of ethanol in the gas that are lower than those corresponding to equilibrium, hence less ethanol is evaporated than would otherwise be the case. In contrast, in open industrial systems, the working volume is much greater than for the other scales tested, consequently, the average free passage of the bubbles is also much longer, and much higher degrees of equilibrium are reached.

In the particular case of acetic fermentation, the aim is to minimize the losses of ethanol through evaporation, in the interests of process efficiency in the industry. Therefore, from the point of view of equipment design, it would be of interest to prevent equilibrium between the liquid and gaseous phases from being reached; in other words, to aim for the lowest possible coefficient of equilibrium.

On this basis, and considering the results shown in Table V, it can be affirmed that semi-closed and closed systems are more efficient, probably due to the levels of aeration used in each case.

In fact, in closed systems the only outflows of gas from the system are those needed to release excess pressure; what would in other processes be interpreted as a lack of liquid-gas equilibrium conditions should in this case, be interpreted as the recirculation of volatile compounds.

From the point of view of the model for evaporation proposed, it can be observed that in the case of industrial fermentors (10,000 L capacity), the theoretical predictions coincide with the experimental results (ϵ = 1); in other words, the gaseous phase leaves the equipment in full equilibrium with the liquid phase, thus confirming the general validity of the model. In the pilot plant scale experiments,

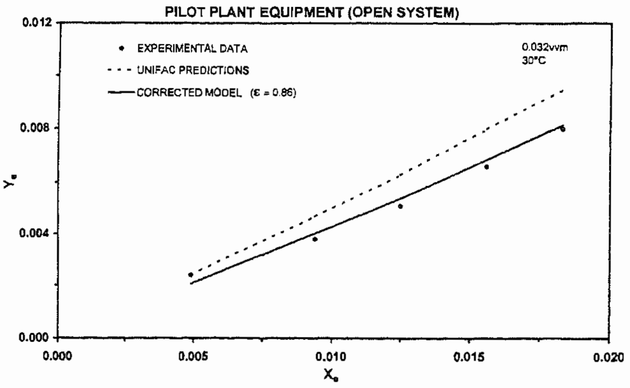

Figure 10. Experimental data, UNIFAC predictions and corrected model data for pilot plant scale open system (0.032 vvm and 30°C).

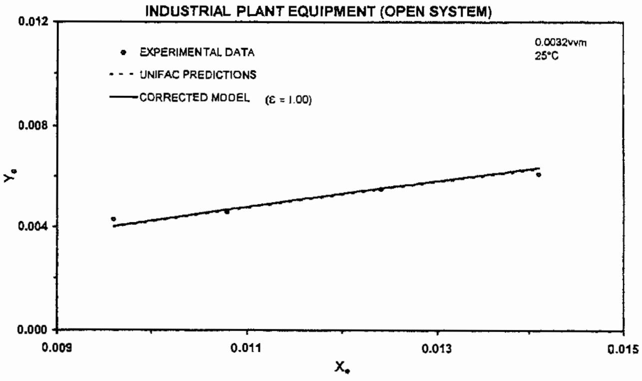

Figure 12. Experimental data, UNIFAC predictions and corrected model data for industrial plant scale open system (0.0032 vvm and 25°C).

Table V. Values obtained for the coefficient ε in the different equipment used in the experimentation, and regression of the experimental data vs. the theoretical predictions, after applying the coefficient ε.

Scale	Volume (L)	System	Temp. (°C)	Air. (vvm)	ε	R^2
Laboratory	5	Open	26	0.05	0.75	0.982
	5	Semi-closed	26	0.05	0.47	0.956
	5	Open	26	0.2	0.66	0.995
	5	Semi-closed	26	0.2	0.58	0.970
Pilot Plant	1,000	Open	30	0.032	0.86	0.992
	1,000	Closed	28	0.2	0.28	0.919
Industrial plant	10,000	Open	20	0.0032	0.97	0.998
	10,000	Open	25	0.0032	1.00	0.998

the open system provides a coefficient ϵ of 0.826, while in the closed system, this coefficient is 0.28; this confirms the need to introduce into the calculations the parameter ϵ for the degree of equilibrium reached. Finally, the laboratory scale experiments give results further from the equilibrium than in the case of open systems; this is because, in the latter cases, the flow of gas introduced into the fermentor comes partially saturated with volatile compounds and, as it passes through the medium, it removes a much smaller quantity of ethanol than if it entered completely pure. In short, in this case, two stages of equilibrium are established: the desorption column and the fermentor itself, the value of the degree of equilibrium (ϵ) corresponding in this case to that provided by the second stage.

CONCLUSIONS

1. The general model of evaporation proposed is valid for the prediction of the liquid-gas equilibrium, with sufficient accuracy, in acetic fermentation equipment.
2. It is necessary to introduce the coefficient of the "degree of equilibrium," to compare different systems of acetic fermentation tested—open, semi-closed, and closed.
3. Closed systems are the most suitable for industrial purposes, because these show the lowest degree of equilibrium; therefore, this type of equipment has the lowest evaporation loss.

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NOMENCLATURE

a_{kl}	interaction parameter between the groups k and l
$-(di/dt)_E$	rate of evaporation of the component i (mol/h)
E_k	weighted interaction parameter of the group k
F_k	auxiliary calculation function of the group k
G_E	excess Gibbs energy (Kj/mol)
l_i	weighted surface-volume parameter
MV	molar volume of gas (L_{gas}/mol_{gas})
MW_i	molecular weight of the substance i (g/mol)
P_i	partial pressure of the component i in the gaseous phase
P_i^0	vapor pressure of the pure component i
q_i	surface parameter of the molecule i
Q	aeration rate of the system
Q_l	surface parameter of the group l
r_i	volume parameter of the molecule i
R	gas constant (0.082 atm L/mol K)
R_l	volume parameter of the group l
S	stoichiometric factor
T	operation temperature (K)
X_i	molar fraction of the component i in the liquid phase
X_l	fraction of the group l in the mixture
Y_i	molar fraction of the component i in the gaseous phase.
Z	number of coordination

Greek letters

ϵ	equilibrium factor
ϕ_i	fraction of volume of the molecule i
γ_i	activity coefficient of the component i in the liquid phase
γ_i^C	configuration part of the activity coefficient for the pure substance i
γ_i^R	residual part of the activity coefficient for the pure substance i
Γ_k	function of activity of the group k in the mixture
${}^i\Gamma_k$	function of activity of the group k in the pure component i
θ_i	surface fraction of the molecule i
θ_k	surface fraction of the group k
Ψ_{kl}	residual fraction of interaction

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