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MASS TRANSFER IN FERMENTATION PROCESSES

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Abstract. The peculiarities of anaerobic fermentation processes with the accumulation of dissolved ethyl alcohol and carbon dioxide in the culture media are considered in the article.

The solubility of CO_2 is limited by the state of saturation in accordance with Henry's law. This, with all else being equal, limits the mass transfer on the interface surface of yeast cells and the liquid phase of the medium. A phenomenological model of the media restoration technologies based on the unsaturation index on CO_2 is developed. It is shown that this restoration in the existing technologies of fermentation of sugar-rich media occurs, to a limited extent, in self-organized flow circuits, with variable values of temperatures and hydrostatic pressures, due to the creation of unsaturated local zones.

It is shown that increasing the height of the media in isovolumetric apparatuses leads to an increase in the levels of flow circuits organization and to the improvement of the desaturation and saturation modes of the liquid phase and intensification of mass transfer processes. Among the deterministic principles of restoring the saturation possibilities of the media, there are forced variables of pressures with time pauses on their lower and upper levels. In such cases, the possibilities of short-term intensive desaturations in full media volumes, the restoration of their saturation perception of CO_2, and the activation of fermentation processes are achieved. This direction is technically feasible for active industrial equipment.

The cumulative effect of the action of variable pressures and temperatures corresponds to the superposition principle, but at the final stages of fermentation, the pressure and temperature values are leveled, so the restoration of the unsaturation state slows down to the level of the bacteriostatic effect. The possibility of eliminating the disadvantages of the final stage of fermentation by means of programmable variable pressures is shown.

Key words: mass transfer, fermentation, hydrodynamics, pressure, temperature, solubility, gas phase.

МАСООБМІН В ПРОЦЕСАХ БРОДІННЯ

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Анотація. Розглянуто особливості перебігу процесів анаеробного бродіння з накопиченням в культуральних середовищах розчинених етилового спирту і діоксиду вуглецю. Показано, що збільшення висоти середовищ в ізооб'ємних апаратах приводить до обмеження рівня невпорядкованості циркуляційних контурів, що вказує на перспективи організованої детермінованої циркуляції. Цей напрямок можливо вважати першим кроком в удосконаленні апаратів і технологій бродіння, тоді як наступний етап має стосуватися регульованих впливів у формі використання змінних тисків у сполученні зі змінними температурами для гарантованого обмеження станів насичення зброджуваних середовищ на CO_2 з відповідними технологічними і економічними наслідками. Це позбавляє недоліків завершальної стадії бродіння, на якій нівелюються показники інтенсивності циркуляційних контурів і потреби в динаміці охолодження середовищ. Досягнення такого стану припиняє процеси їх локальних переходів до ненасичених станів. Зростаючі осмотичні тиски в сукупності з насиченістю середовищ діоксидом вуглецю на фізичному рівні приводять до біостатичних ефектів.

Ключові слова: масообмін, бродіння, гідродинаміка, тиск, температура, розчинність, газова фаза.

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Introduction. Formulation of the problem

The process of anaerobic fermentation is accompanied by endogenous synthesis of carbon dioxide and ethanol that enter the fermented medium through biological membranes. Without going into the peculiarity of the intracellular transportation of these substances at the molecular level, let's dwell on the peculiarities of their transition to a liquid medium. It is important that alcohol dissolves in water in random proportions unlike carbon dioxide because its solubility is restricted by Henry's law by which the saturation constant c_s is proportional to the partial pressure P of the gas phase:

$$c_s = kP . \qquad (1)$$

Since the situation relates not to a mixture of gases, but only to CO_2, then it is believed that the specified partial pressure is the general pressure at each point of the fermented medium. The Henry constant k in condition (1) reflects the physical properties of the liquid and gas phases and the influence of the thermodynamic parameter of the temperature. In this connection, in the graphic representations of the condition (1), the values of c_s are given by isotherms (Fig. 1), and in this case:

$$t_1 < t_2 < t_3 < t_4 . \quad (2)$$

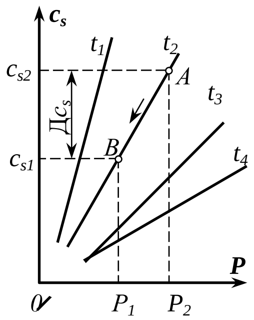

Fig. 1. Graphic representation of Henry's law in the form of equation (1)

The fact that the fermentation machines are of considerable dimensions, its hydrostatic component significantly influences the overall pressure index. Therefore, in each coordinate h we have:

$$P = P_0 + \rho g h , \quad (3)$$

where P_0 is the pressure of the gas phase over the medium; c is the specific mass of the liquid phase; h – altitude coordinate in terms of the liquid phase.

We note that the indices of pressures P_0 and hydrostatic pressures $\rho g h$ are often proportional, so they should be considered collectively.

From the moment the liquid phase is saturated with carbon dioxide, dynamic equilibrium is violated, and the dispersed gas phase is formed, with the continuity of the medium ruptured from the zone with the smallest to the zone with the greatest hydrostatic pressure. Under the action of the Archimedean forces, the dispersed phase passes with the formation of flow circuits of unstable structure and energy potentials. With gas forming at greater and greater depths, the gas-retaining capacity of the medium increases with increasing energy potentials in the flow circuits.

The formation of a dispersed gas phase means that the saturation state is reached in the liquid phase, which restricts, and under certain conditions stops the mass transfer of CO_2 between the yeast cells and the medium. Literary sources [1–5] point out the negative effects of elevated concentrations of dissolved carbon dioxide on fermentation dynamics. So, at the CO_2 pressure 0.1 MPa, the reduction of yeast growth is recorded, and at the pressure of 0.8 MPa and the temperature 15°C, fermentation stops. Although these data do not give a complete picture of the physical state of the medium, they confirm the significant effects of dissolved CO_2.

Analysis of recent research and publications

An overview of literary sources leads to the conclusion about the availability of information about characteristics of anaerobic and aerobic processes of fermentation, physical-chemical properties of gas-liquid media, features of osmotic pressure, etc.

So in the study [1], the stages of alcohol fermentation under the conditions of primary fermentation of wine materials are considered. The composition of the input material streams of grape must has certain characteristics, but the classical principles of alcohol fermentation, including that in the presence of saprophytic microflora, are preserved.

The paper [2] presents the results of analytical studies concerning the colligative properties of fermentable sugar-containing media. The dynamics of osmotic pressure changes, and the transformation of organic substances are registered.

The publication [3] is devoted to a general technical and thermodynamic approach to the intensification of heat and mass exchange processes in food technologies. It presents modern technologies based on the use of closed energy circuits and discrete impulse influences.

The interconnections between transformations of organic substances and osmotic media pressures are investigated in [4, 5], with the corresponding mathematical formalizations obtained.

In the publication [6], the peculiarities of transformations in fermentable media are analyzed, accompanied by thermodynamic transformations at the level of entropy estimates.

Modern ideas in the technology and physiology of wort fermentation [7] are supplemented by including the description of methods of obtaining non-alcoholic beer.

Publications [8, 9] are devoted to the physical and physical-chemical principles of the existence of the biological world, and the work [10] refers to the peculiarities of the synthesis of bioenergetic potentials of ethanol in the agro-sector.

The research [11] is devoted to the features of industrial fermentation processes. The publication [12] provides information about the intensification of anaerobic fermentation technology.

However, there are no attempts to evaluate the possibilities for the intensification of mass transfer processes due to the interaction of the alternating pressures and the levels of solubility of the gas phase.

The aim of the study. In the form of a local conclusion, let’s point out the practicability of limiting the periods of media’s saturated states. Obviously, this is how the processes of fermentation are completed, and therefore the purpose of this study is to look for the ways of creating technologies to restore media according to the parameter of the unsaturated state.

The research task is connected with the creation of phenomenological (theoretical) justification of the possibilities of regenerating the culture media of anaerobic fermentation to renew the modes of the active mass transfer with yeast cells and renew their activity.

Research materials and methods

The basis for our research is the gas solubility law and, related to it, Pascal's law about hydrostatic pressures, and regularities concerning the conditions of continuity of media.

The well-known provisions concerning the hydrodynamics of gas-liquid media and the effects of flow circuits on the mass transfer processes are used. Some conclusions were formulated basing on the phenomenological generalizations.

Results of the research and their discussion

With the state of the medium physically complying with the condition (1), we turn to the search of transition processes modes, by which the flowing concentration of carbon dioxide c will be less than this indicator in the saturation state with the representation of the condition:

$$c < c_s . \quad (4)$$

Achieving this proportion means a decrease in the medium's resistance to the mass transfer on the boundary where the phases are separated, and the renewal of the latter. When a dispersed phase appears in the liquid phase of a fermented medium, it is an indication that the boundary state in the form $c = c_s$ is reached and cannot be exceeded. However, a move towards a decrease of the saturation constant is possible due to the decrease in the pressure P_0 in the gas over-liquid phase, which will be immediately reflected in the full volume of the gas-liquid medium. In Fig. 1, this process is represented by the line segment AB on the isotherm t_2 with a decrease of the saturation constant by the Δc_s value:

$$\Delta c_s = c_{s2} - c_{s1} . \quad (5)$$

The system's double response to the pressure reduction will be the growth of gas-retaining capacity, firstly, due to the formation of an additional dispersed gas phase at the level Δc_s and, secondly, due to the expansion of the existing gas phase. However, at the level of the condition (4), the situation does not improve, since the liquid phase remains in the saturation state. The fulfilment of the condition (5) means reducing the amount of dissolved CO_2 in the medium in accordance with the final pressure P_1 at this stage. It is important that, during the transition of pressure from P_2 to P_1, the medium is in the saturation state.

Thus, the pressure reduction does not improve the situation of mass transfer at the interface of phase separation, but reducing the concentration of dissolved gas leads to a decrease in osmotic pressure for this component. This feature is practically the only technical opportunity to organize oscillations of osmotic pressures at the expense of physical influences. Obviously, as for the fermentation dynamics, this result can be considered positive.

The outgassing process lags somewhat behind the pressure drop dynamics due to the inertial properties of the media. But the limited time pause after reaching the given P_1 leads to the case of c_{s1}, which is the completion of the first stage. Its important feature is that, in the isothermal process and in the linear relationship between the value c_s and P, only a range of pressure changes in the form of $P_2 - P_1$ matters, and not the absolute pressure values.

A fast pressure increase in the over-liquid gas phase by the difference:

$$\Delta P = P_2 - P_1 \quad (6)$$

leads to a positive disturbance of the equilibrium at the phase interface, because the condition (4) is fulfilled and the liquid phase of the medium becomes unsaturated. In this case, the initial driving factor of the mass transfer process is determined by the condition:

$$\Delta c_{s(i)} = c_{s2} - c_{s1(i)} , \quad (7)$$

where index (i) is the index of the initial parameter of the value.

It is obvious that the flowing concentration of dissolved CO_2 is variable in the form of the time function. The same holds true for the driving factor $\Delta c_s = \Delta c_s(t)$.

The final value of the second stage corresponds to:

$$c_{s(f)} = c_{s2} . \quad (8)$$

The existence of the second stage means the possibility of renewal of active mass transfer of CO_2 at the interface of phase separation.

This phenomenological representation of the physics of mass transfer processes between the liquid phase and yeast is a certain approximation to the real processes, since it relates to a static point of view on the medium, in which the influence of geometric parameters, the presence of flow circuits with the peculiarities of their kinematic characteristics etc. are not taken into account. However, an important conclusion from this is that overcoming barriers of saturation in fermentable media requires processes in which self-sustaining or organized pressure changes are achieved. The self-sustainability of the latter is connected with the presence of vertical flow circuits and the manifestation of a gravitational field in the form of hydrostatic pressures and Archimedes forces.

The passing of the dispersed gas phase is accompanied by the appearance of ascending gas-liquid streams and, at the same time, the descending streams with unsteady parameters as for their structure and kinematics. Although the level of instability of such characteristics is important, however, in general assessment of the hydrodynamics of media, the presence of flow circuits is positive for a number of aspects, including the creation of variable pressures in the volumetric zones of the ascending and descending parts of the flow circuits. It is obvious that these are hydrostatic pressures that decrease in the medium's ascending streams with the formation of an additional dispersed gas phase. In the descending parts, the increase in hydrostatic pressures increases the solubility of CO_2. In this case, the hydrodynamics of the medium with the parameters of gas-holding capacity and the reduced rate of the gas phase are secondary phenomena associated with the life of microorganisms and with CO_2 synthesis. The intensity of fermentation and the volume of the culture medium determine the velocity and volume of the generated gas phase. Thus, this regulates how the geometry of the medium influences (by means of the technological apparatus's geometry) the medium's gas-holding capacity and energy potentials, the power of flow circuits and the possibilities of restoring the liquid phase properties in the saturation and desaturation modes.

The processes of fermentation in given cycles are uninterrupted. This leads to an increase in total pressures in the over-liquid volume of the apparatus, followed by the operation of the safety valves and the removal of excess CO_2 outside. This process is accompanied by a partial desaturation in full volume, but the flowing concentration still corresponds to the state of saturation with new pressure indicators. The subsequent gradual increase in the pressure in the over-liquid volume only occurs at the expense of the further desaturation of the medium with the fulfillment of the condition $c = c_s$. The transition to a relation $c = c_s$ is only possible with the forced increase of pressure in the over-liquid volume as well as in the volume of the gas-liquid medium. In this case, the use of carbon dioxide for such an increase is undesirable due to the increased saturation on the phase interface. However, a rapid pressure increase in the system provides transition to the desired condition $c < c_s$. This positive effect on the medium is combined with the effects of the presence of flow circuits in accordance with the superposition principle.

The presence of cooling systems in the fermentation apparatuses is due to the need to stabilize the temperature of the fermented medium at the nominal level by diverting biological heat in accordance with the Gay-Lussac equation:

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2 + 169\,\text{kJ}. \quad (9)$$

When we know the fermentation dynamics, the power of the diverted heat is estimated. The intensity of heat loss is influenced by the coefficients of heat exchange, heat transmission, heat transfer surface, and temperature difference. The heat transfer coefficients on the heat exchange surfaces are determined by the hydrodynamic states of the liquid phases and depend on the intensity of the flow circuits created, among other things, by cooling the medium.

With the shirt cooling system (Fig. 2), in the peripheral zones, the downstream flows of the liquid phase are formed. Their temperature, without clearly defined boundaries, is 5–7°C lower than the corresponding parameter in the central part of the medium.

The presence of a temperature gradient in the cross-sections of the medium, in conjunction with the flow circuits, further increases the solubility level of carbon dioxide. The effects of local cooling zones and variable hydrostatic pressures are represented by the dependences in Fig. 3.

The saturation parameters c_{sA} at the input of the downstream part of the flow circuit at a temperature $t_A = t_3$ and at the pressure P_1 correspond to point A on the graph. Let us assume that, along with the continuous downstream motion of the local zone, the temperature in it will decrease to the value $t_B = t_1$ under the condition of an isobar process with the value $c_{sB} = t_1$ reached at P_1 = const. However, in the case of circulation, the hydrostatic pressure $P \neq$ const, and in the lower part of the apparatus, the final pressure is P_2. That is why, in the isothermal process at $t_A = t_3$, the increase in solubility would be equal to Δc_{ss}, and at the medium's temperature $t_B = t_1$, the increase in solubility becomes Δc_{sts}.

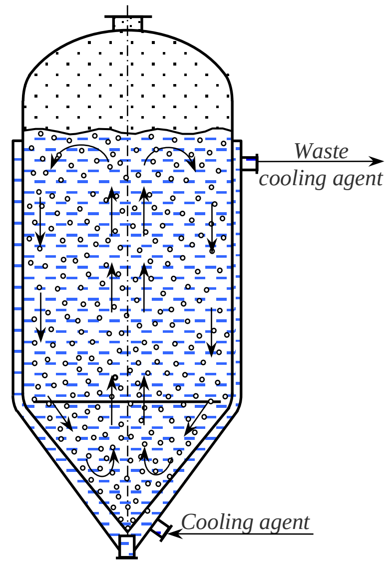

Fig. 2. Circulation circuits in the fermentation apparatus

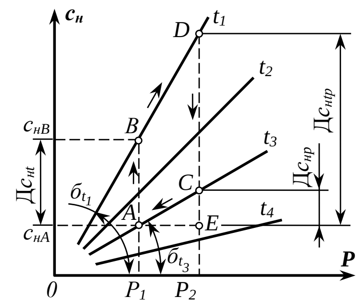

Fig. 3. Graphic dependences for determining the reducing potential of solubility CO_2

All else being equal, the influence of temperatures on the solubility of CO_2 is shown by the tangents of the angles of the isotherm to the horizontal axis:

$$\mathrm{tg}\alpha_{t_1} = \frac{c_{sB}}{P_1}; \quad \mathrm{tg}\alpha_{t_3} = \frac{c_{sA}}{P_1}, \quad (10)$$

where α_{t_1} and α_{t_3} are angles of inclination corresponding to isotherms 1 and 3.

On the basis of the condition (10), the saturation constant of the medium, when the values of temperature t_1 and pressure P_2 are known at the point D, is determined:

$$c_{sD} = P_2 \mathrm{tg}\alpha_{t_1} \quad (11)$$

and the overall result of the recovery potential of the solubility of CO_2:

$$\Delta c_{stp} = c_{sD} - c_{sA} = P_2 \mathrm{tg}\alpha_{t_1} - P_1 \mathrm{tg}\alpha_{t_3} = P_2 \frac{c_{sB}}{P_1} - c_{sA}. \quad (12)$$

Approbation of the research results. Approbation of theoretical studies was carried out on fermentation machines of "Brewery on Podil". It showed a decrease in the fermentation time by 15–17%.

Conclusions

1. Thus, it can be called a fact that the existence of zones for the restoration of solubility is associated with such components as flow circuits of gas-liquid media, cooling systems and hydrostatic pressures. It is important that the factors mentioned depend on the geometrical parameters of the technological devices, which is confirmed in modern sizes and ratios of cylindrical conical devices (CCD) for the fermentation of media in the brewing industry.

2. The increase in the height of the media in the isovolume apparatuses leads to limiting the irregularity level of the flow circuits, which shows the prospects of organized deterministic circulation. This direction can be considered the first step in the improvement of apparatuses and technologies of fermentation. The next step should deal with regulated influences. They are exerted through using alternating pressures in combination with variable temperatures to ensure limiting the saturation states of digestible media on CO_2 with the corresponding technological and economic consequences.

3. Due to such conditions it is possible to get rid of the disadvantages of the final stage of fermentation, at which the indicators of the intensity of flow circuits and the need for the dynamics of cooling of the media are leveled. Achieving such state discontinues the processes of their local transitions to unsaturated states. Increasing osmotic pressures in combination with the saturation of media with carbon dioxide on the physical level leads to biostatic effects.

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