Study on the in-situ coupling process of fermentation, extraction and distillation for biobutanol production: process analysis

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Abstract. The transfer process of the in-situ coupling process of fermentation, extraction and distillation for biobutanol production was discussed from a theoretical point of view. The existence of temperature gradient in the extraction section was proved. The force of solute in the extracted liquid was discussed. And the mass transfer mechanism and impetus of the FEDIC process was analyzed. The theoretical analysis could provide a foundation for the following research.

1. Introduction
In recent decades, the decline of petroleum reserves, the surge in population and the degradation of the environment have initiated great interest in the development of renewable biofuels. Among the biofuel alternatives, biobutanol, as the main product of acetone-butanol-ethanol (ABE) fermentation, is one of the most potential replacement fuels [1-3]. However, ABE fermentation suffers a strong end-product inhibition which has adversely affected the economics of commercial production [4-6].

The main limitation of ABE fermentation is the toxic effect of butanol on microorganisms which leads to the low solvent productivity. The cells are completely inhibited at 10-15 g/L of biobutanol [7-9]. It is not economically competitive for butanol recovery by conventional distillation [7, 10]. Therefore, various in-situ butanol removal technologies (such as extraction [10-12], gas stripping [13, 14], adsorption [8] and pervaporation [15,16]) from the fermentation system have been used to mitigate butanol inhibition and improve productivity. Although there has been significant progress in the integration of fermentation and product recovery techniques, there are various challenges before the commercial applications of these technologies. For example, in-situ solvent extraction fermentation has been proposed as one of the most promising approaches for minimizing butanol inhibition and increasing product titer. However, the high price of the extracting agent and the subsequent cost of extracting agent recycling have prevented its application on a large scale [10, 11].

In order to reduce the energy consumption for ABE recovery and extracting agent recycling, we introduced an in-situ coupling process of fermentation, extraction and distillation (abbreviated as FEDIC process) for biobutanol production [17]. In this process, a concentrated ABE solution could be obtained by heating the upper part of the extracted liquid (light phase) at the same time of the extractive fermentation. Since only a small part of the extracted liquid needed to be heated and the corresponding cooling operation was avoided, it is expected that the FEDIC process could reduce the energy consumption. In this paper, the transfer process of the coupling process was discussed.
2. Materials and methods

2.1. Materials
Acetone, butanol and ethanol were analytical grade reagents and used as received. Castor oil (hydroxyl value > 155, acid value: about 1.5 mg KOH/g, density: 0.96 g/ml) was obtained from the local market.

2.2. Experimental Equipment

Figure 1. Experimental set-up of the FEDIC process. (1) Temperature controller; (2, 16) Thermocouple; (3, 15) Heating mantle; (4) Extracting agent; (5-12, 17, 20) Thermometer; (13) Feed inlet; (14) Fermentation broth; (18) Condenser; (19) Vacuum system interface; (21) Gas inlet; (22) Outlet port; (23) Magnetic stirring bar; (24) Magnetic stirrer with heating.

As shown in Figure 1, the experimental set-up is a 1.5-meter tall tank with a distillation system at the top and several thermometers (or thermocouples). It is divided into three sections, i.e. fermentation section, extraction section and distillation section. A heating mantle around the fermentation section is
to keep the fermentation broth at a constant temperature, and another one around the distillation section is for heating the upper part of the extracted liquid (light phase) to gain the ABE solution. The distillation section was connected with a vacuum system, whose pressure was controlled by a vacuum pump adjusted according to the vacuum degree. The fermentation section had a gas inlet for introducing air to stir the solution in the tank.

2.3. Experimental Procedure
To evaluate the FEDIC process for ABE recovery from a dilute solution, the process was conducted using a model ABE solution obtained by mixing water, butanol acetone and ethanol. Initial concentrations of butanol in the model solution were 12 g/L. Concentrations of acetone and ethanol used for formulation of the ABE model solution followed the ratio typically found in batch ABE fermentations, 6:3:1 (butanol/acetone/ethanol). About 3 L of ABE model solution was added to fill the fermentation section and was kept at a constant temperature with a modest magnetic stirring. And about 10 L of castor oil, as the extracting agent, was introduced to fill the extraction section. Then the experimental set-up was sealed and vacuumized using a circulating water pump. Air was introduced from gas inlet 21 for stirring the fermentation broth and the extracted liquid. Then the upper part of the extracted liquid was heated to a constant temperature by the heating mantle 3, and the temperature of different sections was recorded. The temperature field of the FEDIC process was also measured by a FLIR T400 infrared camera.

3. Results and discussion
The set-up of the FEDIC process was divided into three sections, i.e. fermentation section, extraction section and distillation section. By heating the upper part of the extracted liquid (light phase in the distillation section) a concentrated ABE solution was obtained. In this process, it is a prerequisite to ensure the temperature of the fermentation broth in a suitable range to maintain the biological activity of the microorganisms for cyclic utilization of the fermentation broth, since the overhigh temperature would cause the microorganisms to die.

Figure 2 shows the temperature field of the FEDIC process, measured by an infrared camera after running time 24 h. The results indicated that the fermentation broth and the lower part of the extracted liquid could maintain a low temperature while the distillation section maintained a high temperature.

![Figure 2](image-url)

**Figure 2.** The temperature field of the FEDIC process with magnetic stirring (without gas stirring, DT = 80 °C, BT = 27.5 °C, running time 24 h).
According to the theories of extraction and pervaporation we deduced the mechanism of the FEDIC process, as shown in Figure 3: (1) ABE migrates from the fermentation broth to the liquid-liquid phase interface by molecular diffusion and convection. (2) ABE passes through the phase interface from the fermentation broth to the extracted liquid by molecular diffusion. (3) ABE continues upward diffusing by molecular diffusion and convection. (4) ABE reached high temperature zone and then were vaporized. The bubbles grow, rise to the gas-liquid phase interface and pass through the phase interface. (5) ABE vapor continues upward migrating and is condensed.

Our further experimental results have proved that the fermentation broth and the lower part of the extracted liquid could maintain a low temperature. Thus the FEDIC process was achievable from the point of the temperature field. Here, the existence of temperature gradient in the extraction section was proved using mathematical methods.

The right graph in Figure 3 is the simple graph of the extraction section. T_A and T_B are the temperatures of A zone and B zone, respectively. When the system reaches steady state, there apparently exist T_A \geq T_B, since the upper part of the extracted liquid was heated. And T_B is higher than room temperature.

Assuming T_A=T_B, which means that there does not exist temperature gradient and the heat transfer between A zone and B zone is the equal. And because of T_B > room temperature, B zone must transfer heat to the outside world (heat loss \( q > 0 \)) according to the second law of thermodynamics. It will lead to the decreasing of T_B. Thus T_B \neq T_A, which contradicts the hypothesis (T_A=T_B). It suggests that the assumption is incorrect.

So T_A>T_B, the temperature gradient must exist. And it suggests that the heat would transfer downward.

The mass transfer impetus of ABE include concentration gradient, temperature gradient and density gradient: (1) There must be a concentration gradient since the extracted components were continuously separated out in-situ and keeps in a unsaturated state. (2) The higher the temperature was, the higher the molecular diffusion coefficient were. And the higher the temperature was, the higher the partition coefficient of some extracting agents (such as oleyl alcohol and iso-octanol) were. (3) The density gradient exists since the density of ABE is lower than the used extracting agent. And the density gradient can produce buoyancy to ABE.

Here we mainly discuss the mass transfer in the extracted liquid of the FEDIC process, since the other sections were similar with the conventional extraction and distillation.

The force diagram of ABE in the extracted liquid is shown in Figure 4. ABE is regarded as a small ball with a diameter d. The ball is subject to three forces, namely gravity G, buoyancy F_b and resistance F_r, written respectively as

![Figure 3. Graph for the process analysis of the FEDIC process.](image-url)
\[ G = mg = \frac{\pi}{6} d^3 \rho g \]  
\[ F_b = \frac{\pi}{6} d^3 \rho_e g \]  
\[ F_r = \xi \frac{\pi}{4} d^2 \rho_e \frac{u^2}{2} \]  

where \( m \) is the mass of the ball (ABE), \( g \) is the gravitational acceleration, \( \rho \) is the density of the ball, \( \rho_e \) is the density of the extracted liquid, \( \xi \) is resistance coefficient and \( u \) is the instantaneous velocity of the ball.

Thus the force of the ball is described by the equation
\[ F = \frac{\pi}{6} d^3 \rho_b g - \frac{\pi}{6} d^3 \rho_e g - \xi \frac{\pi}{4} d^2 \rho \frac{u^2}{2} \]  

Newton’s second law gives
\[ F = ma \]  

where \( a \) is the acceleration of the ball.

Thus:
\[ F = \frac{\pi}{6} d^3 \rho_b g - \frac{\pi}{6} d^3 \rho_e g - \xi \frac{\pi}{4} d^2 \rho \frac{u^2}{2} = ma \]  

At the bottom of the extraction section \( u \) is very small and \( F > 0 \). The ball will accelerate upwards. The resistance \( F_r \) increases with the increasing of the instantaneous velocity \( u \). When \( F = 0 \), the ball reaches uniform rising state. But for the FEDIC process, it can hardly take place since there are concentration gradient, temperature gradient and density gradient.

In addition, the instantaneous velocity \( u \) can be considered to be produced by the force \( F \) and concentration gradient, thus
\[ u = v_1 + v_2 \]  
where \( v_1 \) and \( v_2 \) are the velocity produced by the force \( F \) and concentration gradient, respectively.

\[ a = \frac{dv_1}{dt} \]  

where \( t \) is time.

\[ J = c(v_2 - v_1) = -D \nabla c \]
where $J$ is diffusion flux of the component with only consideration of concentration gradient, $v_2$ is the velocity of the component, $v_1$ is the average velocity of the fluid, and $c$ is the molar concentration of the component. $\nabla$ is the notation for the gradient. $D$ is the diffusion coefficient of the component, also known as the Fick diffusion coefficient.

Thus the mass transfer in the extracted liquid has been preliminarily made clear from what has been discussed above.

In addition, the mass transfer mechanism of the FEDIC process was similar with that of pervaporation. The extracting agent used in the FEDIC process could be regarded as a thick layer of liquid film, while pervaporation usually used a solid-supported membrane. Compared with the pervaporation membrane, the liquid film had several significant advantages such as fast mass transfer, easy automatization, cheapness, convenient operation and low operation cost. So the FEDIC process was a promising separation approach.

4. Conclusion

In this paper, the transfer process analysis of the in-situ coupling process of fermentation, extraction and distillation for biobutanol production was carried out. The existence of temperature gradient in the extraction section was proved. Thus the fermentation broth and the lower part of the extracted liquid could maintain a low temperature while the upper part of the extracted liquid was maintaining a high temperature. And the mass transfer mechanism and impetus of the FEDIC process was analyzed, which proved that the FEDIC process was achievable in theory. However, there are still many unknowns about the FEDIC process. So the comprehensive experimental and theoretical researches should be conducted in the future. In addition, it is also a valuable work to investigate the similar applications in other fermentation process and wastewater treatment.

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