



# A POROUS PERMEABLE WALL CONTAINING FERMENTOR FOR IN-SITU EXTRACTIVE RECOVERY OF BIOBUTANOL FROM DILUTE FERMENT LIQUORS

László Kótai<sup>[a,b]\*</sup> and István Gács<sup>[a]</sup>

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A new type of bioreactor containing a porous permeable wall to recover the biobutanol produced in anaerobic ABE fermentation processes is presented. The ferment liquor is contacted with an organic solvent and the butanol in the fermentation liquor distributes between the organic phase and the ferment liquor. The butanol containing solvent located at one side of the permeable wall is in a diffusion equilibrium with a same kind of auxiliary solvent with lower butanol concentration located at the other side of the permeable wall. Due to the concentration difference, butanol diffuses from one side of the wall to the other side. The concentration difference is kept to be constant by continuous removal of the butanol from the auxiliary solvent phase in which the butanol concentration is always lower than in the extractant phase but much higher than the butanol concentration in the ferment liquor phase. In this way, the primary extractant solvent contacting the ferment liquor is only a transmitting media between the ferment liquor and a small volume of the auxiliary solvent separated with the permeable wall. The energy demand of the distillation to remove the butanol from the auxiliary solvent is less than the energy demand of the direct butanol recovery from the ferment liquor or from the extractant phase. The new reactor provides a possibility to develop a continuous fermentation technology, continuous sugar adding and butanol recovery operating far below the toxic limit and inhibition conditions of butanol in the ferment liquor.

Corresponding Author  
Fax: +36-23-376-456  
E-Mail: kotail@chemres.hu;

[a] Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1025, Pusztaszeri u. 59-67, Budapest, Hungary;

[b] Deuton-X Ltd., H-2030, Érd, Selmeci u. 89.

## Introduction

Biobutanol (n-C<sub>4</sub>H<sub>9</sub>OH) is the most promising biofuel of the near future. It can be produced by means of the so-called anaerobic ABE (acetone-butanol-ethanol) fermentation not only from food-grade resources like corn, but from various waste materials of the agriculture and of the food production.

Although biobutanol has excellent fuel properties compared to ethanol, its production cost is very high because of its accumulation in the ferment liquor leading to the death of the fermenting enzymes even at low (~2%) concentration. It means that large amount of wastewater formation (98%) occurs and the recovery of the product from the ferment liquor in a usual way (distillation) requires a large amount of energy. Conclusively, the increase of the butanol concentration and the produced butanol/used energy ratio, respectively are the key factors for increasing the feasibility of the production process. Increased productivity can be achieved by the so-called in-situ extractive fermentation in a new type of instrument reported here.

This fermentor separates the formed biobutanol via a special porous permeable wall system. In this paper the construction of the extractive fermentor system is described, and the basic elements of the technology are discussed.

## Results and Discussion

### General consideration of two-phase extractive fermentation

From the start of the fermentation process, the butanol concentration is allowed to increase up to the toxic limit ( $C_F^*$ , kg/kg ferment liquor) in the ferment liquor phase, meanwhile the concentration of the butanol in the extractive solvent ( $C_E^*$ ) contacted with the ferment liquor can be written as

$$C_E^* = K_B C_F^* \quad (1)$$

where  $K_B$  is the distribution coefficient between the ferment liquor and the extractant.

It means that the amount of the butanol formed can be written as

$$\sum X_B = F C_F^* + E C_E^* \quad (2)$$

where  $F$  and  $E$  are the amounts of the ferment liquor (in kg) and extractive solvent (in kg), respectively. By feeding the same type of auxiliary solvent into the smaller reactor space separated from the fermentor with a permeable composite wall (Fig.1), the concentration difference at  $t=0$  time immediately induces a diffusion process which terminates when the concentrations are equalized in the extractant solvents located in the two separated reactor spaces.

If  $V_1 > 0$ , then  $C_E$  definitely less than  $C_E^*$ , because the  $C_E = C_A$  concentration can be expressed as

$$C_E = \frac{EC_E^*}{E + \rho_1 V_1} \quad (3)$$

where  $\rho_1$  is the density of the organic extractant and  $V_1$  is the volume of the extractant in the separated reactor space. Since the product of  $\rho_1 V_1 > 0$ , thus  $E + \rho_1 V_1 > E$  and

$$C_E < C_E^* \quad (4)$$

When higher volume for  $V_1$  is selected, larger difference between  $C_E$  and  $C_E^*$  can be reached. Let a given  $V_1$  be the auxiliary solvent volume and the appropriate surface area of the permeable wall between the  $E$  and  $A$  phases be  $S_1$ . The amount of the butanol from the  $C_A$  phase is supplied by diffusion through  $S_1$  surface. In this case,

$$V_1 \frac{dC_A}{dt} \leq E \frac{dC_E}{dt} \quad (5)$$

This process would result continuously decreasing  $C_A$ ,  $C_E$  and  $C_F$  values. However, if the rate of the fermentation in the  $F$  ferment liquor can supply the amount of butanol removed, then the two key parameters determining the amount of the formed and removed butanol will be the amount of the ferment liquor,  $F$ , and the amount of the auxiliary solvent,  $A$ , because

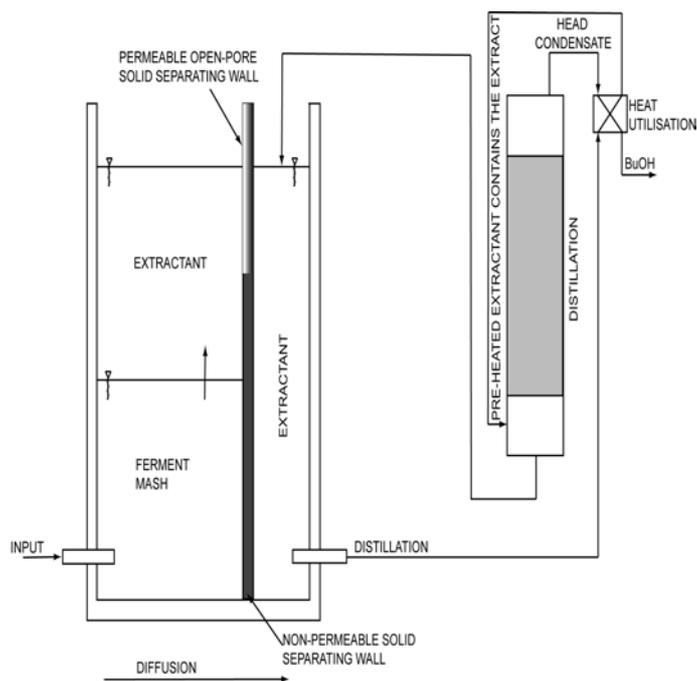
$$-V_1 \frac{dC_A}{dt} \leq F \frac{dC_F}{dt} \quad (6)$$

and because the  $C_E = C_A$  and  $C_F = K_B C_E$  conditions are valid.

These considerations have been taken by neglecting the effect of the back-diffusion of the extractant solvent. Since not only the butanol can move through the porous permeable wall from one side to the other, but the extractant solvent molecules can also diffuse from the lower butanol concentration phase to the higher butanol concentration phase as well. During the design of the reactor this phenomenon has to be taken into consideration.

### The construction of the fermentor

The main construction element of the fermentor is a vertical wall which divides the reactor into two non-equal parts. The larger part of the reactor space is used as a common two-phase fermentor in which the ferment liquor ( $F$ ) and the extractant solvent ( $E$ ) are located. The extractant ( $E$ ) is a nonmiscible solvent which does not inhibit the enzymatic processes<sup>1</sup>. The same kind of auxiliary solvent ( $A$ ) used as secondary extractant is located in the smaller separated part ( $V_1$  volume) of the fermentor. The separating wall is divided into two parts. The extractant are generally have lower density than the ferment liquor, thus the extractants are the upper phases. The bottom part of the separating wall is made from a non-permeable material and this part completely prevent the mixing and contacting the ferment liquor and the auxiliary solvent. The upper part of the separating wall is made from a porous permeable composite material<sup>2</sup>, which ensures the diffusion of the butanol



**Figure 1.** An in-situ two-phase extractive fermentor with porous permeable wall construction

between the extractant solvent and auxiliary solvent by the concentration difference as a driving force. The equilibrium between the ferment liquor and auxiliary solvent is mediated by the extractant phase.

As it can be seen in Fig. 1, the reactor part contains a butanol recovery column attached to the auxiliary solvent tank. This column is a usual distillation column, however, it has a heat utilization system in order to preheat the output of the auxiliary solvent containing butanol and to cool down the recycled butanol-free auxiliary solvent stream.

The temperature and amount of the recycled auxiliary solvent can control the temperature of the ferment liquor via appropriate selection of the thicknesses of the non-porous heat-conducting and the porous heat-insulating parts of the vertical separating wall.

Since the upper porous and the bottom non-porous parts of the separation wall are made from heat-insulating composite material and a heat-conducting metallic material, respectively, it is obvious, that the magnitude of the heat transfer via the porous and non-porous parts is not equal. During the extraction process not only butanol mass transfer but heat transfer also occurs from the ferment liquor to the extractant phase. Two other factors also can decrease the temperature of the ferment liquor without outer heat supplement. Firstly, the optimum temperature of the ferment liquor is around 37 °C in the ABE fermentation<sup>3</sup>. Thus, without heat supplement the continuous addition of sugar solution at room temperature would decrease the ferment liquor temperature.

Secondly, the amount of the ferment liquor is preferably larger than the amount of the extractant phase, thus the wall surface in contact with the ferment liquor is also larger than the fermentor surface contacting the extractant. Consequently, the heat loss toward the outer environment is larger from the ferment liquor phase. In order to avoid secondary heat transfer from the warmer extractant phase to the ferment liquor phase, namely to the opposite direction of the heat and mass transfers due to the butanol diffusion from the ferment liquor to the extractant phase, the temperature difference between the two phases has to be minimized.

The temperature of the ferment liquor has to be adjusted to 37°C. In this way the temperature of the extractant should be lower than 37 °C. This condition can easily be adjusted by appropriate selection of the separating wall construction materials with different heat conducting properties and with the thickness of the upper and bottom wall.

Using this type of heat utilization systems the energy balance of the butanol recovery is much more economic than in the case of a simple distillative butanol recovery from dilute (<2%) ferment liquor, especially if the solvent selected has a high distribution coefficient (Table 1) for butanol recovery.

**Table 1.** Butanol distribution coefficients and heat capacities of solvents used as extractants in butanol recovery at 25 °C

Solvent	$K_B$ value	$C_p$ , J/g.K
Oleyl alcohol	3.5	2.32
Heptanal	13.0	2.15
Oleic acid	3.0	2.80
Hexanol	7.8	2.32
Octanol	6.7	2.34
Ethyl butyrate	2.9	1.96
Water	-	4.18

Taking into consideration the parameters<sup>4</sup> shown in Table 1, for the selection of an appropriate solvent, the  $C_A$  concentration in the quasi-equilibrium state is always much higher than the  $C_F$  concentration values. Conclusively, not only the absolute amount of the heated solvent ( $A$ ) will be less than the absolute amount of the ferment liquor ( $F$ ), but the relative amount of the heated  $A$  to recover one kg of butanol will be less than the heated amount of ferment liquor to recover the same amount of butanol.

Furthermore, the heat capacity values of the organic solvents (see Table 1) are generally only the half to the heat capacity of the water, thus the used thermal energy is much less to heat this mixture up to the boiling point than in case of the aqueous ferment liquor. In the design of the biobutanol production by two-phase extractive fermentation by using porous membrane wall, for an expected productivity the determination of the  $V_1$  volume of the separated reactor space is one of the key parameters.

The ratio of the volume of the two reactor spaces ( $V_1/V_2$ ) unambiguously determines the required surface area of the wall at a given  $F/E$  ratio. The relative amount of the ferment liquor ( $F$ ) and extractant ( $E$ ) is determined by the diffusion surface of the wall which has to ensure the same value of the butanol stream ( $B$ ) from the extractant to the auxiliary solvent which is formed in the ferment liquor and is removed from the auxiliary solvent. If the diffusion rate of the butanol from the  $E$  phase to the  $A$  phase through the porous wall is equal with the rate of butanol removing from the  $A$  phase and the rate of butanol formation in the  $F$  phase, supposing that the distribution of the butanol between the  $E$  and  $F$  phases are faster than its formation rate, then the process is in a quasi equilibrium.

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## References

- Griffith, W. L.; Compere, A. L.; Googin, J. M. *Dev. Ind. Microbiol. Ser.* **1983**, *24*, 347; Ishii, S., Taya, M., Kobayashi, T., *J. Chem. Eng. Japan.* **1985**, *18*, 125.
- Ernő Tamics, Zsuzsanna Bajnóczki, and Pradeep K. Sharma, *J. Chem. Asia*, **2012**, accepted to publish; Roy, Della M., *Mater. Res. Soc. Symp. Proc.* **1989**, *137*, 179.
- Komarova, L. I., *Mikrobiologiya* **1955**, *24*, 208; Voget, C. E.; Mignone, C. F.; Ertola, R. J., *Biotechnology Lett.*, **1985**, *7*, 607; McNeil, B., Kristiansen, B., *Biotechnol. Lett.*, **1985**, *7*, 499; Oda, M., Yamaguchi, S., *Nippon Nogei Kagaku Kaishi* **1948**, *22*, 3; Lepage, C., Fayolle, F., Hermann, M., Vandecasteele, J. P., *J. Gen. Microbiol.*, **1987**, *133*, 103.
- Dadgar, A. M., Foutch, G. L., *Biotechnol. Bioeng. Symp.*, **1985**, *15*, 611.

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