



GLOBAL JOURNAL OF RESEARCHES IN ENGINEERING: C
CHEMICAL ENGINEERING

Volume 19 Issue 1 Version 1.0 Year 2019

Type: Double Blind Peer Reviewed International Research Journal

Publisher: Global Journals

Online ISSN: 2249-4596 & Print ISSN: 0975-5861

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Keywords: 1-butanol, aqueous solution, fermentation, separation.

GJRE-C Classification: FOR Code: 290699



ASSESSMENT OF SEPARATION PROCESSES FOR RECOVERY OF 1-BUTANOL FROM ITS DILUTE AQUEOUS SOLUTION

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Assessment of Separation Processes for Recovery of 1-Butanol from its Dilute Aqueous Solution

Shreya Akshay Thakkar ^α, Atharva Shashank Chikhalikar ^σ & Neha Amol Padwal ^ρ

Abstract- Microbial fermentation yields aqueous solutions with concentrations of 1-3 % by weight of organic compounds. Moreover, the presence of organics in water may lead to hazardous effects on health and the environment. Separation and recovery of these organics from water poses difficulties for industries as several energy-intensive operations such as distillation prove to be uneconomical when compared with the energy content of 1-butanol. Fermentation broth concentrations upto 70 kg/m³ are required to produce an effective liquid-liquid split. The paper aims at assessing several unit operations for recovering 1-butanol from water in terms of their recovery, purity, energy input and evaluating their applicability. Separation processes studied are freeze crystallization, adsorption, pervaporation, reverse osmosis, phase separation using salts and ionic liquids. Some adsorbents were found to be efficient for extracting 1-butanol from the solution. Multiple stages of pervaporation were capable of providing a high purity stream of 1-butanol. Likewise, freeze crystallization and reverse osmosis also offer feasible alternatives to overcome the separation crisis. The ability of ionic liquids and salts to alter the equilibrium even at low 1-butanol concentrations can be potentially utilized for separation. A comparison of these operations reveals that we need to make a compromise between energy efficiency, recovery, and purity.

Keywords: 1-butanol, aqueous solution, fermentation, separation.

Highlights

- Evaluating feasibility of unit operations based on energy, recovery, and purity.
- Based on recovery, freeze crystallization and salting are potential options.
- Adsorption and reverse osmosis were found to be the least energy intensive.
- Hybrid separation processes could be the key to solve separation crisis.

I. INTRODUCTION

1-butanol has a plethora of uses in the manufacture of commodity as well as specialty chemicals. It possesses numerous advantages as a biofuel. Firstly, it has a higher organic content than ethanol

which makes it more compatible to mix with gasoline. Secondly, its energy content is similar to petrol making it a suitable replacement. Moreover, high energy density, low vapor pressure, and low corrosiveness result in easier handling making it a promising bio-fuel ^[1, 2, 3, 4].

1-butanol production on industrial scale occurs via microbial fermentation yielding concentrations of 1-3% by weight. Above concentrations of 2 wt % of 1-butanol, process inhibition occurs, and fermentation is stopped ^[4, 5, 6]. Its separation and recovery is a crucial step in the industry. Although distillation is the most widely practiced separation process, its energy requirement is comparable to the energy content of 1-butanol rendering it uneconomical ^[7, 8]. Much higher fermentation broth concentrations are required to produce an effective liquid-liquid split ^[9]. This paper assesses alternative separation methods for 1-butanol recovery such as freeze crystallization, adsorption, pervaporation, reverse osmosis and phase splitting using salts or ionic liquids, and evaluates them on the basis of recovery, purity, and energy-input.

We have considered a concentration of 20 kg/m³ 1-butanol in aqueous solution and a flow rate of 1000 kg/hr for the continuous unit operations for calculations. Uniform basis for each unit operation evaluated ensures that this paper provides an effectual comparison amongst the separation methods studied.

II. FREEZE CRYSTALLIZATION

Freeze crystallization (FC) is a separation method based on the difference in melting points of the components in the mixture. It is a relatively newer method which has not found much application in the industry due to difficulty in operation. There is a considerable difference in latent heat associated with evaporation and fusion. While distillation exploits the former which is much higher, FC is based on the latter leading to lower energy requirements ^[8]. In the last few decades, the principles of FC have been applied for the purification of water ^[10, 11].

FC is based on the solid-liquid equilibrium of the mixture. As the temperature is lowered, the component with higher melting point crystallizes to give a product with very high purity ^[12] resulting in a change in concentration of the solution. A typical equilibrium

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diagram showing the cooling temperature on the Y-axis and composition of the solution in the liquid phase is depicted in Figure I. This phase diagram enables us to

calculate the quantity of crystals formed using lever rule and the amount remaining in the liquid phase and its composition.

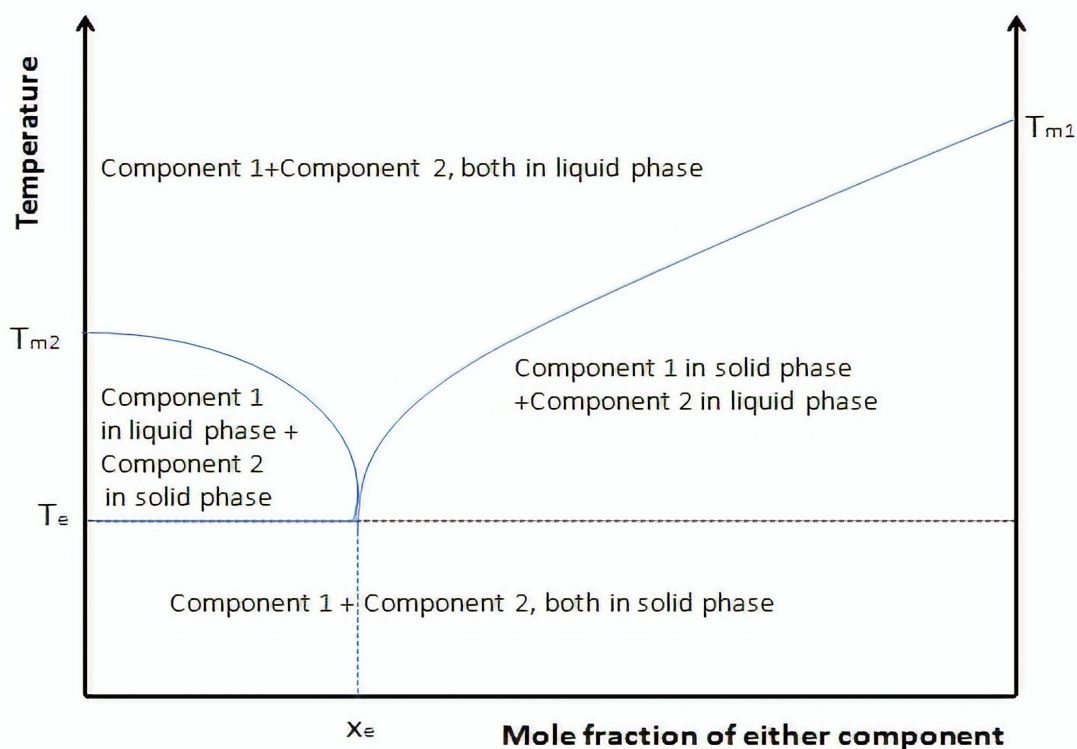


Figure I: Solid-Liquid phase equilibrium for binary mixtures (where T_{m1} and T_{m2} represent melting point temperatures of component 1 and 2 respectively; T_e represents eutectic temperature, and X_e represents eutectic composition)

The above concept was used to calculate the mole fraction of 1-butanol remaining in the liquid phase after crystallization of water from the aqueous solution.

The solid-liquid equilibrium data for this system is represented in Figure II ^[13].

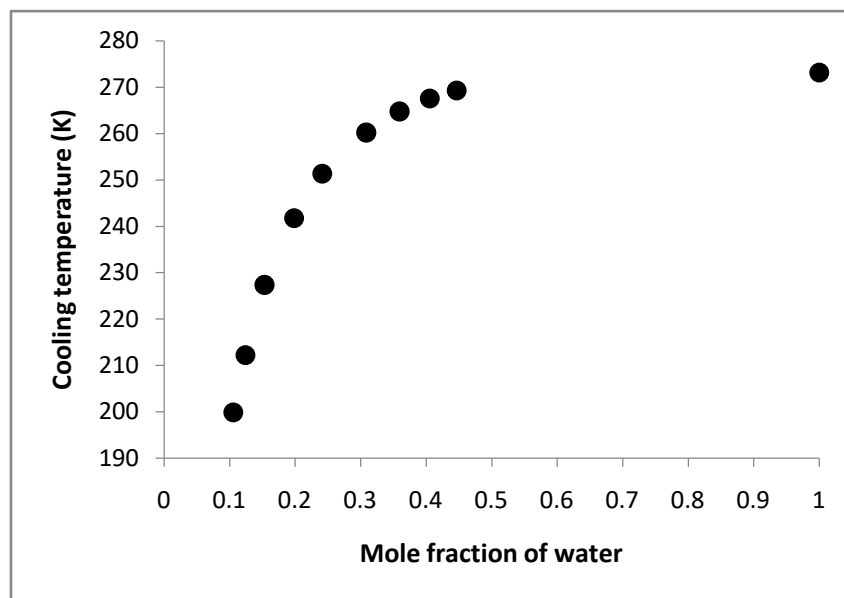


Figure II: Solid-Liquid equilibrium data for 1-butanol and water mixture

The pure component melting point of water is 273.16 K and that of 1-butanol is 183.3 K. Since the data in Figure II is above 183.3 K, it represents right-hand side of the curve in Figure I where component 1 would be water and component 2 would be 1-butanol.

$$y = 2694x^3 - 2993x^2 + 1160x + 108.5 \quad (I)$$

Using equation (I) and applying lever rule, the variation of 1-butanol concentration in the liquid phase

The data points between 269.28 K to 199.89 K were regressed to obtain cooling temperature in K (y) as a function of mole fraction of water in the liquid phase (x) with $R^2 = 0.998$

with cooling temperature was calculated and represented in Figure III.

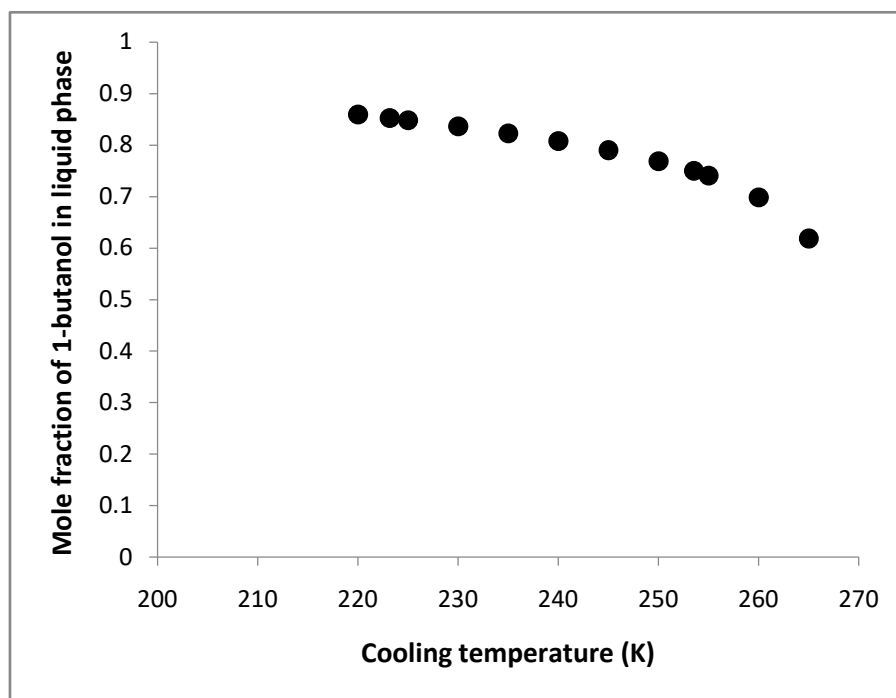


Figure III: Plot of how mole fraction of 1-butanol decreases with an increase in cooling temperature

Cooling to 253.53 K yields a concentration of 0.75 mole fraction 1-butanol in the liquid stream and 99.83% of water fused to form ice. This temperature is attainable, and there is a significant improvement in 1-butanol concentration from an inlet of 0.005 mole fraction to 0.75 mole fraction in the outlet. More concentrated outlet stream can be obtained at lower temperatures. But, it is not feasible to use a cooling agent to attain such low temperatures at an industrial scale. Cooling agents such as liquid nitrogen, solid carbon dioxide or even glycols at very high concentrations can achieve significantly low temperatures but possess handling difficulties.

At 253.53 K, ethylene glycol in water can be used as a cooling agent at a concentration of 45% by weight. Other cooling agents such as propylene glycol brine can be used, but it has very high viscosity. Calcium chloride can also be used but it is highly corrosive^[14] and has a relatively low specific heat^[15].

Hence, the energy requirements for crystallization using 45% by weight ethylene glycol brine were calculated at a cooling temperature of 253.53 K.

Table I: Feed properties assumed for calculations

Feed flow rate (1-butanol+water)	1000 kg/hr
Feed concentration	20 kg/m ³ 1-butanol in water
Feed temperature	293.16 K

Under the conditions mentioned in Table I, the overall heat load on the system is calculated to be 495.05 MJ/hr by energy balance which is equivalent to 24.75 MJ/kg of 1-butanol whereas the combustion enthalpy of 1-butanol is 36 MJ/kg of 1-butanol^[16].

The temperature to which the solution is to be cooled will determine the energy required for crystallization, purity of product and coolant selection. At a higher cooling temperature, ethylene glycol brine at lower concentrations is suitable since it has better heat capacity and lower viscosity. Table II summarizes the ethylene glycol properties required, the energy required to cool the feed and 1-butanol concentration in the liquid phase at various cooling temperatures.

Table II: Effect of cooling temperature on coolant properties, energy requirement, and purity

Cooling temperature (K)	Concentration by % weight of ethylene glycol	Specific heat capacity (kJ/kg K)	Viscosityx1000 (Pa s)	Energy required to cool 1000 kg/hour feed (MJ/hour)	Liquid phase 1-butanol mole fraction in after crystallization
upto 264	35 ^[15]	3.60 ^[15]	6.8 ^[15]	451.04	0.62
upto 253	45 ^[15]	3.31 ^[15]	17.2 ^[15]	495.05	0.75
upto 239	55 ^[15]	3.06 ^[15]	75 ^[15]	558.16	0.81

Table II suggests that a compromise among energy requirement, ease of handling and purity needs to be made. Maintaining sub-zero temperatures and handling a large quantum of ice crystals are the key challenges posed to the application of FC for 1-butanol and water separation. But, high recovery and lower energy requirements than conventional distillation process provide an incentive for encouraging pilot plant trials. With the advancement in technology to overcome the practical difficulties in operation, FC is expected to be a promising technology for separating low concentrations of 1-butanol in water.

III. PERVAPORATION

Pervaporation is a novel membrane technology which has a dual effect of two processes combined in one set-up: namely reverse osmosis and membrane gas separation ^[17]. Pervaporation consists of a selective membrane through which different entities present in a liquid mixture diffuse according to their permeabilities through the particular membrane ^[18]. Thus, the mechanism of separation is the difference in the affinities of the components in the mixture for the specific membrane ^[19]. The process is purposefully carried out at a very low pressure to ensure that the components evaporate and are collected on the downstream as purified gaseous products which then can be removed with the help of vacuum pump or with the use of chillers ^[17, 18, 19].

Pervaporation being a membrane-based process, some factors such as permeabilities, flux, separation factors depend upon the type of membrane

utilized. Separation of 1-butanol and water has been performed by a variety of membranes each with one modification over another to get higher flux and permeate concentrations. According to Vane ^[19], poly dimethyl siloxane (PDMS) is a widely used membrane for separation. Vane ^[19] effectively tested various PDMS membranes with certain modifications such as integration of membrane with octadecyldiethoxymethylsilane, and PTFE (poly tetra fluoro ethylene) or PP (polypropylene) which were found to have higher separation factor and selectivity than usual PDMS membranes. Liu et al. ^[20] performed a separation of water and 1-butanol using ceramic membranes. Li et al. ^[21] introduced a new membrane: tri-layer PDMS for effective separation of 1-butanol and water. Wang et al. ^[22] took the PDMS one step ahead by generating a zeolite, PDMS matrix membrane for the separation which helps in generating better interface compatibility. Fouad and Feng ^[23] evaluated the properties of PDMS membrane filled with silicalite particularly adapted to separate 1-butanol and water.

A recent advance in membrane materials consists of hyper-branched structure to enhance the properties of the membranes like low package density, negligible crystallinity, etc ^[24, 25, 26]. Bai et al. ^[26] developed a highly efficient modification of PDMS membrane which consisted of cross linkers in the form of hyper branched polysiloxane. Due to the novelty of the membrane and performance characteristics depicted, this membrane was utilized for further calculations.

Table III: Stage-wise parameters and values

Parameter	Stage I	Stage II	Stage III
Temperature (K)	313.16	318.16	363.16
1-butanol Permeability (mol.m/(m ² .s.Pa)	8.88*10 ⁻¹¹	8.04*10 ⁻¹¹	4.69*10 ⁻¹¹
Water Permeability (mol.m/(m ² .s.Pa))	1.34* 10 ⁻¹¹	1.34*10 ⁻¹¹	1.34*10 ⁻¹¹
Permeate Pressure (Pa)	1333.22	1333.22	133.22

The water permeability remains the same while, the 1-butanol permeability decreases with temperature, as seen from the data in Table III. In case of pressure driven pervaporation, the concentration of a component at the permeate side would depend upon the permeability at that temperature and activity coefficient of the component ^[18]. The driving force in such cases is the pressure difference between the feed and the permeate stream which is kept maximum to obtain better separation.

In the case of linear systems where permeability value is assumed to be constant, flux equation for binary mixture can be written as follows:

$$J_A = Q_A(\gamma_A * x_A * P_A^* - y_A * P_2) \quad (II)$$

In a similar manner, we can write equations for the other component.

Where, J_A is the flux of component A through the membrane, Q_A is Ratio of permeability to membrane thickness for component A, γ_A is Activity coefficient of component A, x_A is Mole fraction in feed of component A, y_A is the mole fraction of A in permeate, P_A^* is Vapour pressure of component A at the given temperature, P_2 is Permeate Pressure.

For the estimation of activity coefficient, Redlich-Kwong model was used to calculate Gibb's free energy of both liquid and gas phase which were used to estimate the values of fugacity coefficients in the liquid phase as well as gaseous phase respectively. Further, modified Raoult's law was applied to determine activity coefficient at Vapor-Liquid Equilibrium data points which then was regressed concerning 1-butanol mole fraction to obtain activity coefficient at any concentration.

Pressure ratio and modified selectivity has been defined in the following manner: ^[18]

$$R_A = \frac{P_2}{\gamma_A * P_{A2}^*}; R_B = \frac{P_2}{\gamma_B * P_{B2}^*} \quad (III)$$

$$\alpha' = \frac{Q_A * \gamma_A * P_A^*}{Q_B * \gamma_B * P_B^*} \quad (IV)$$

Separation factor in any pervaporation set-up is defined as follows:

Where R_A is Pressure Ratio for component A, R_B is Pressure Ratio for component B, α' is Modified selectivity.

$$\beta = \frac{\frac{c_{iP}}{1-c_{iP}}}{\frac{c_{if}}{1-c_{if}}} \quad (V)$$

With the knowledge of permeate pressure (P_2), the initial conditions and the permeabilities, equations (III), (IV) and (V) can be solved simultaneously to obtain the permeate composition of 1-butanol at different stages. The results obtained are stated in Table IV.

Table IV: Pervaporation results

Parameter	Stage I	Stage II	Stage III
Temperature (K)	313.16	318.16	363.16
Permeate Mole Fraction of 1-butanol (y_b)	0.21	0.81	0.81
Permeate Flux of 1-butanol (kg/m ² s)	0.017*10 ⁻³	0.45*10 ⁻³	1.6*10 ⁻³
Permeate Flux of water (kg/m ² s)	0.016*10 ⁻³	0.025*10 ⁻³	0.21*10 ⁻³

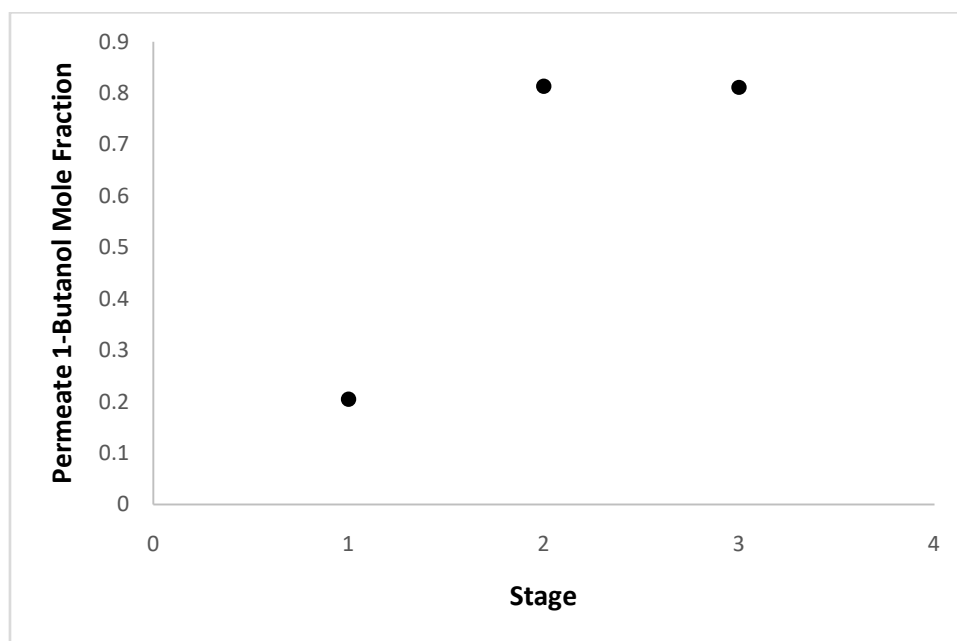


Figure IV: Plot of permeate 1-butanol mole fraction versus Stage number

With the increase in the number of stages from 1 to 2, the output mole fraction of 1-butanol increased. Further increase in the number of stages reduces the output concentration but increases the flux as seen in Table IV. The initial increase in the output concentration can be attributed to the rise in the temperature of the feed and high activity coefficient of 1-butanol at the feed concentration, which is not the case for the subsequent stage.

The flux of 1-butanol was found to increase along with the process temperature because of the fact that, with an increase in temperature, the saturated pressure of both the components increase while the permeate pressure remains constant. This increases the driving force to which the flux is proportional as shown in Equation (IV). Thus, the flux increases with increase in temperature, even though the permeability decreases.

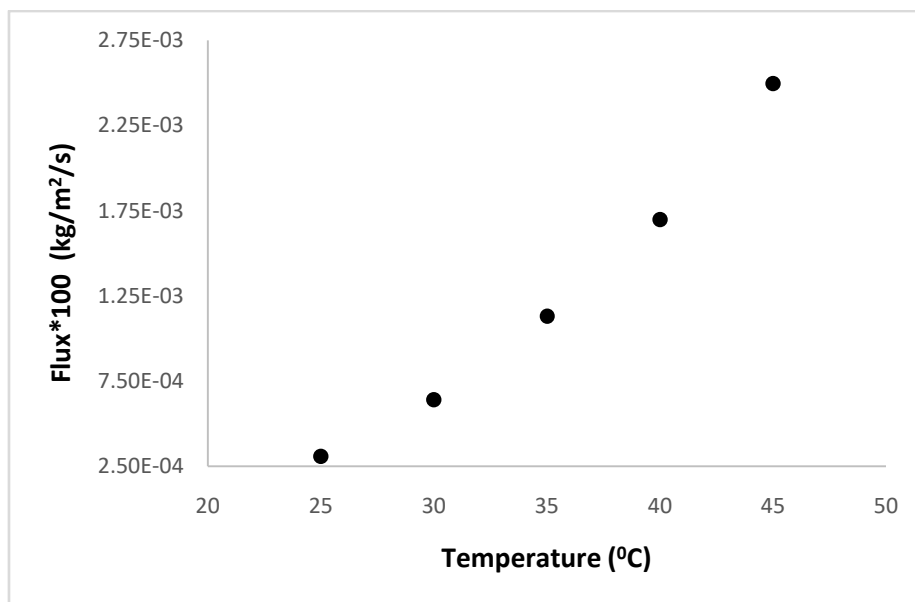


Figure V: Plot of flux variation with temperature

Pervaporation resulted into permeate mole fraction of about 0.82 at the second stage. Moreover, pervaporation is an environment-friendly alternative which separates the components without affecting

microbe activity and growth, which allows for in-situ operation. Thus, pervaporation seems to be a practical alternative for separation of 1-butanol from the water.

IV. REVERSE OSMOSIS

Reverse osmosis (RO) provides an efficient solution for the removal of low molecular weight organic compounds from their low concentration aqueous solutions. Several studies have been conducted to separate organic compounds from their dilute aqueous solutions with the help of reverse osmosis [27, 28, 29].

Rejection of compounds by the membrane is dependent on the combination of membrane materials and solute to be separated. Several membranes have been fabricated and qualified for seawater desalination, but the membranes most suitable for desalination are not always useful for organic-aqueous separation [30]. Solute and solvent diffusivity through the membrane is used to describe the influence of solvent, solute and membrane interaction on the performance of the membrane. Notably two commercially available RO membranes have been studied extensively for 1-butanol separation from water, namely the cellulose acetate membrane and the composite polyamide membrane.

Different scientists have attempted to correlate the rejection coefficients for cellulose acetate and aromatic polyamide membranes with polar and steric parameters, molecular size or with solubility parameters [29, 21, 32, 33]. The rejections obtained by cellulose acetate membrane for organic-aqueous solutions are relatively low, especially for low molecular weight organic compounds [28]. Polyamide membranes have exhibited rejection rates as high as 98% and have a potential application in 1-butanol-water separation [34, 35].

For estimation of rejection and permeate fluxes at target feed concentration and flow rate, the MSCB2521 R99 spiral-wound aromatic polyamide membrane was considered, and the preferential sorption-capillary flow model was employed. Alvarez et al. [36] provided the required membrane and feed parameters, pure water permeability, and 1-butanol transport parameter ($D_{AM}/K\delta$) through the membrane. Table V reports the above values.

Table V: Constants, membrane and feed parameters (where: a=solute; b= water)

Parameter	Value	Parameter	Value
Temperature (T)	298.16 K	Equivalent hydraulic diameter (d_h)	9.6×10^{-4} m
1-butanol transport parameter ($D_{AM}/K\delta$)	1.91×10^{-6} m/s	Molar volume of pure water (V_w)	18.07 m ³ /kmol
Feed density (ρ)	1000 kg/m ³	Permeability of pure water (A)	7.83×10^{-12} m ³ /s m ² Pa
Feed viscosity (μ)	0.001 Pa s	Diffusivity of 1-butanol in water (D_{ab})	9.6×10^{-10} m ² /s [37]
Feed flow rate (Q)	1 m ³ /hr	Effective area tangential to the feed flow (A_t)	0.001 m ²

Kimura et al. have proposed an empirical equation for the estimation of osmotic pressure as a function of 1-butanol concentration [38].

$$\pi = -\frac{RT}{V_w} \ln \left(\frac{\frac{1000-c_b}{M_w} - \frac{2c_b}{M_g}}{\frac{1000-c_b}{M_w} - \frac{c_b}{M_g}} \right) \quad (VI)$$

Where, T and R are the temperature and universal gas constant respectively; V_w is the molar volume of pure water; and M_w and M_g are the molecular weights of water and 1-butanol, respectively; π is the osmotic pressure.

Schock and Miquel's correlation, established for spiral-wound modules, was used to estimate the mass transfer coefficient of 1-butanol in the concentration polarization boundary layer (k_a) [39].

$$Sh = 0.065 Re^{0.875} Sc^{0.25} \quad (VII)$$

Where Sc is the Schmidt number ($\mu/\rho D_a$), Re is the Reynolds number ($d_h v \rho / \mu$), and Sh is the Sherwood number ($k_a d_h / D_a$). d_h is the equivalent hydraulic diameter; k_a is the mass transfer coefficient for species 1-butanol, v is the tangential flow velocity, D_a is the diffusion coefficient for species A, μ is the solution viscosity, and ρ is the solution density.

The concentration of solute on membrane surface was then determined by film theory.

$$C_{a2} = C_{a1} \exp \left(\frac{N_b}{k_a C_1} \right) \quad (VIII)$$

Where C_{a1} is the feed 1-butanol concentration; C_{a2} is the concentration of 1-butanol on the membrane surface; N_b is the molar flux of water; C_1 is the molar density of the feed solution.

The flux of water and 1-butanol through the membrane were then estimated using preferential

sorption-capillary flow model and hence the solute rejection. Solute rejection, water flux as well as the solute flux increased with the applied pressure. Figure VI depicts the dependence of solute rejection on the applied pressure.

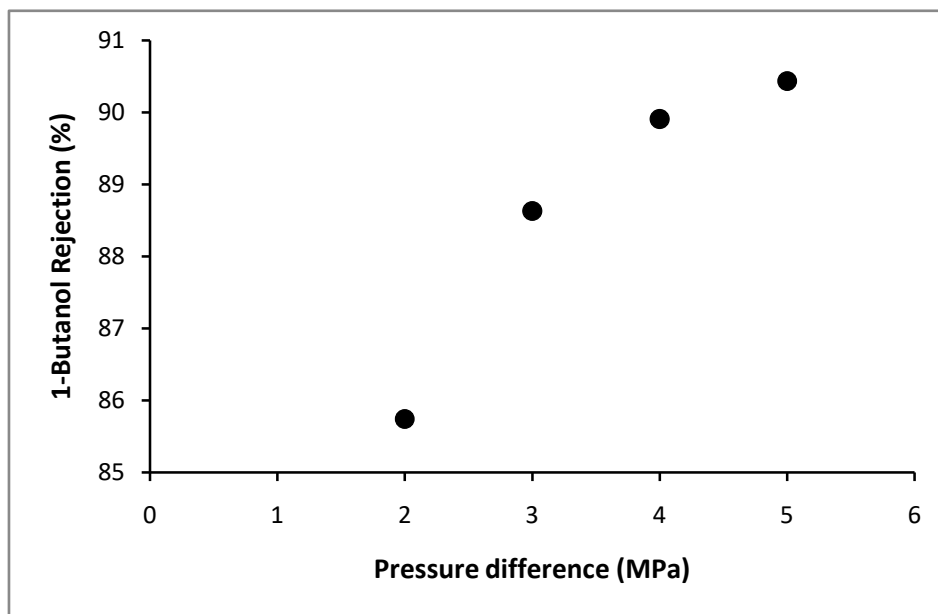


Figure VI: Plot of 1-butanol rejection (%) versus Pressure difference (MPa)

1-butanol rejection increased with pressure difference on account of a stronger dependence of molar water flux on the pressure difference than that of the molar solute flux.

Despite the restriction on rejection due to its strong dependence on applied pressure, higher rejection to some extent can be achieved by customizing specific membrane and feed parameters such as leaf width, spacer thickness, porosity, temperature among others. In a typical seawater reverse osmosis plant, 3 to 10 kWh of electric energy is required to produce one cubic meter of freshwater ^[40]. This energy requirement when calculated for our feed concentration comes out to be around 1.8 MJ/kg of 1-butanol. This value is much lower compared to the energy requirement of most other separation processes. Thus, reverse osmosis can provide us with an energy-efficient alternative, compared to the traditional unit operations for 1-butanol recovery.

V. ADSORPTION

1-butanol separation from aqueous solutions and its recovery by adsorption is an energy efficient method with promising results ^[7]. Multiple adsorbents like activated carbon, zeolite, amberlite have been studied for 1-butanol adsorption from water at very low concentrations of 1-butanol. Various studies have been

performed to experimentally demonstrate the effectiveness of adsorbents for this separation ^[7, 41, 42].

Abdegagh et al.^[7] found that Activated carbon(AC) F-400 was the most effective adsorbent amongst the adsorbents: ZSM-5, AC F-600, NaY, Silicalite, and multi-walled carbon nanotubes studied by them. Their study on the kinetics of adsorbents indicated that AC F-400 and AC F-600 had the fastest adsorption kinetics among others. In an adsorbent screening study by Milestone and Bibby^[41], Zeolite: ZSM-5 with 4% alumina was found to have the highest adsorption capacity amongst ZSM-5 adsorbents with different concentrations of alumina. Raganati et al. ^[42] observed that adsorption capacity of 1-butanol on Amberlite XAD4, Amberlite XAD7, and Zeolite Y increased with temperature and maximum adsorption capacity was found at 318.16 K when temperatures were varied from 298.16 K to 318.16 K.

In this assessment, we have used the equilibrium data for adsorption from the above studies and calculated the 1-butanol concentration in the rejected stream. The calculations were performed for five adsorbents: ZSM-5 with 4% alumina, Amberlite XAD4, Amberlite XAD7, Zeolite Y, and AC F-400. Conditions mentioned in Table VI were used to calculate 1-butanol concentration in the rejected stream in case of a batch type contact operation.

Table VI: Feed and adsorbent parameters

Amount of Feed	1000 kg
1-butanol concentration in feed	20 kg/m ³
Adsorbent mass required	300 kg
Initial concentration of 1-butanol in adsorbent	0 kg/m ³

Calculations were done for a single stage adsorption model by simultaneously solving the material balance equations and the adsorption isotherm equations. Table VII depicts the results.

Table VII: Capacity of various adsorbents

Adsorbent	Temperature (K)	Isotherm equation *	Concentration of 1-butanol in rejected stream (kg/m ³)
ZSM-5 with 4% alumina	Room temperature	$y = 0.079x^{0.082}$ #	4.48
Amberlite XAD4	318.16	$y = 57.12x / (1 + 0.21x)$ [42]	1.37
Amberlite XAD7	318.16	$y = 152.2x / (1 + 0.2x)$ [42]	0.46
Zeolite Y	318.16	$y = 43.92x / (1 + 0.18x)$ [42]	1.79
AC F-400	Room temperature	$y = 500x / (1 + 2130.5x)$ ##	0.18
* y represents amount of 1-butanol adsorbed per unit mass of adsorbent and x represents concentration of 1-butanol in solution			
# This equation has been obtained by regressing the data from work of Milestone and Bibby [42]			
## This equation has been obtained by regressing the data from work of Abdehagh et al. [7]			

The Table VII allows us to conclude that AC F-400 has the highest adsorption capacity for 1-butanol from the water. The time constant (time required for the 1-butanol concentration to vary by a factor of 0.6321) was reported to be 8.2 minutes for AC F-400 by fitting the experimental results in the study by Abdegagh et al. to the model obtained from Lagergren's pseudo-second order equation for adsorption kinetics. This indicates that AC F-400 also shows very high adsorption kinetics, making it a suitable choice of adsorbent for separation of 1-butanol from water [7].

The desorption of 1-butanol needs to be studied, if we want to evaluate the recovery by this process. Abdegagh et al. experimentally evaluated the recovery of 1-butanol on desorption on AC F-400. According to their study, it is possible to recover 84% of the total 1-butanol adsorbed via thermal desorption process. [43]. AC F-400 is a suitable adsorbent for 1-butanol separation of water since it possesses high

adsorption capacity, favorable kinetics and allows desorption of 1-butanol with significant recovery.

The concentration of 1-butanol in the rejected stream varies considerably with a change in mass of adsorbent: AC F-400 as indicated by Figure VII.

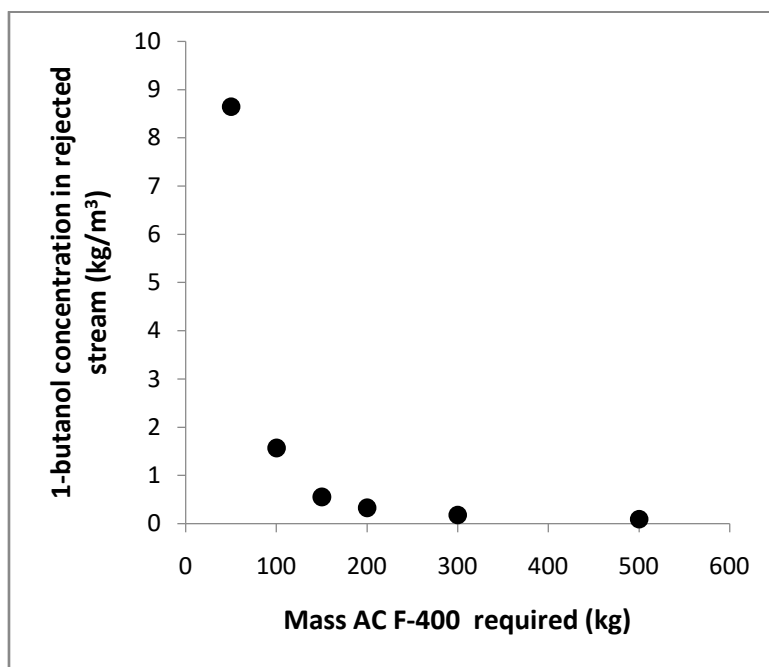


Figure VII: Plot of 1- butanol concentration in rejected stream versus Mass of adsorbent required

It is seen from Figure VII that the 1-butanol concentration in the rejected stream drastically drops with the increase in mass of adsorbent. Hence, enhanced recovery can be obtained with higher mass of adsorbent. The improvement in desorption recovery can be achieved by lowering the cold trap temperature which would increase the energy requirement and subsequently, the operating cost ^[43]. The increased amount of adsorbent required would also increase the capital cost. Hence, a compromise is required between cost and recovery while deciding the operating conditions.

Due to unavailability of literature, the energy efficiency of the process using AC F-400 could not be determined. However, Oudshroon et al. have evaluated the energy of adsorption-desorption process to be 1.3 MJ/kg of 1-butanol assuming heat capacity of the adsorbent to be 1 kJ/kg K. ^[44]. An energy requirement of 8.14 MJ/kg of 1-butanol was reported by Qureshi et al. using silicalite as adsorbent ^[45].

Furthermore, adsorption is the only separation technique besides pervaporation which provides for in-situ separation of fermentation broth resulting from ABE fermentation with an energy demand of about 10% of 1-butanol combustion enthalpy ^[46]. Many studies have evaluated the selectivity of adsorption of 1-butanol and its recovery from the fermentation broth using suitable adsorbents ^[7, 43]. Use of adsorption for in-situ recovery of 1-butanol may improve the economics of the fermentation process ^[47]. Hence, adsorption is an efficient separation method for this separation. Lack of literature on desorption has held back the use of

adsorption-desorption process on the industrial scale for separation of 1-butanol.

VI. LIQUID-LIQUID EXTRACTION USING IONIC LIQUIDS

Liquid-Liquid extraction is seen as a potential alternative to energy-intensive techniques for 1-butanol-water separation such as distillation ^[48]. However, conventional liquid-liquid equilibrium techniques utilizing organic solvents as extractive phase, suffer from the fact that, separation is not high enough for concentration as low as obtained from the fermentation broth ^[9]. Moreover, organic liquids used as extractants such as tert-amyl ether, diisopropyl ether, and dibutyl ether result in significant damage and contamination ^[49]. Hence, the focus has now shifted from organic liquids to ionic liquids for extraction of 1-butanol from the water. Ionic liquids are the ones made up entirely of ions. The term ionic liquid is different from ionic solution as in; NaCl with water forms an ionic solution, while molten NaCl is ionic liquid ^[50]. Ionic liquids are advantageous due to various factors such as low vapor pressure, and high thermal and chemical stability ^[48]. Ionic liquids make way for enormous possible cation-anion combinations which can be utilized to prepare task-specific ionic liquids (ILs). However, following concerns should be addressed before selecting an ionic liquid ^[9]:

1. Toxic nature of the extractant.
2. High selectivity (1-butanol).
3. Loss of liquid to the aqueous phase.

Various ionic liquids have emerged in the field of separation, and this paper attempts to review and evaluate some of them based on their potential for separation. Nann et al.^[48], Domaska et al.^[49], Davis et al.^[9], Fadeev et al.^[51], Garcia-Chevez^[52], Ha et al.^[53], came up with various ionic liquids for the separation of water from 1-butanol. Some of them are listed in Table VIII along with their distribution coefficients and selectivity. Distribution coefficient and selectivity are defined as:

$$S = \frac{w_1^{IL} * w_2^{aq}}{w_1^{aq} * w_2^{IL}} \quad (IX)$$

$$D = \frac{w_1^{IL}}{w_1^{aq}} \quad (X)$$

Where w_1 and w_2 denote the mass fractions of 1-butanol and water respectively; the superscripts IL and aq depict the phases rich in ionic liquid and water respectively.

Table VIII: Data of ionic liquids

Sr. No.	Ionic Liquid	Feed Concentration (%wt 1-butanol)	Temperature (K)	Selectivity	Distribution Coefficient with respect to 1-butanol	References
1	1-decyl-3-methylimidazolium tetracyanoborate $[Im_{10.1}]^+[tcb]^-$	<10	308.16	85	8	[48]
2	4-decyl-4-methylmorpholinium tetracyanoborate $[Mo_{10.1}]^+[tcb]^-$	<10	308.16	78	6	[48]
3	1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[Im_{10.1}]^+[ntf2]^-$	<10	308.16	70	7.9	[48]
4	4-decyl-4-methylmorpholinium bis(trifluoromethylsulfonyl)imide $[Mo_{10.1}]^+[ntf2]^-$	<10	308.16	73	6.1	[48]
5	trihexyltetradecylphosphonium tetracyanoborate $[P14,6,6,6][TCB]$	-	308.16	50-903	25-65	[49]
6	1-decyl-3-methylimidazolium tetracyanoborate $[DMIM][TCB]$	-	308.16	45-125	28-48	[49]
7	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[bmim][Tf2N]$	Higher than obtained in ABE fermentation	298.16	10-100	1.4-7.3	[9]
8	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[hmim][Tf2N]$	Higher than obtained in ABE fermentation	298.16	0.3-77	0.2-8	[9]
9	1-butyl-3-methyl-1H-imidazol-3-ium hexafluoro phosphate $[bmim][PF_6]$	2.01	296.16	25.77	0.849	[51]
10	1-octyl-3-methyl-1H-imidazol-3-ium hexafluoro Phosphate $[omim][PF_6]$	2.01	296.16	55.37	0.923	[51]

11	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [hmim][ntf ₂]	1	298.16	120	1.11	[52]
12	tetradecyl(trihexyl)-phosphonium bis-2,4,4-trimethyl pentyl-phosphinate Cyphos 104	1	298.16	55	9.21	[52]
13	Methyltriethyl ammonium octanoate [MTOAOct]	1	298.16	49	11.29	[52]
14	Tetraoctylammonium 2-methyl-1-naphthoate [TOAMNaph]	1	298.16	274	21	[52]
15	1-hexyl-3-methylimidazolium hexafluoro phosphate [Hmim][PF ₆]	6	298.16	37.47	0.967	[53]
16	1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide [omim][Tf ₂ N]	6	298.16	78.89	1.372	[53]
17	1-phenylpropyl-3-methylimidazolium trifluoromethane sulfonate [Pmim][TfO]	6	298.16	4.96	1.046	[53]
18	1-hexyl-3-methylimidazolium tetrafluoroborate [Hmim][BF ₄]	6	298.16	3.906	0.902	[53]
19	1-methyl-3-octylimidazolium tetrafluoroborate omim][BF ₄]	6	298.16	12.24	2.183	[53]

Table IX shows the performance of various ionic liquids in different conditions. Ionic liquids number 5, 6, 7, 11, 14 in the table show exceptional performance amongst the liquids reviewed.

The tie lines and the extraction data of both the phases specified in the papers were utilized to perform mass balance calculations and evaluate the performance of most of the ionic liquids. The tie lines were selected such that they offered the maximum selectivity as well as recovery of 1-butanol. Table IX gives details of the same.

Table IX: Performance of several ionic liquids

Sr. No	Ionic Liquid	1-butanol Concentration in IL phase (wt %)	Water Concentration in IL phase (wt %)	1-butanol Recovery (%)	Ionic Liquid Requirement *1000 (kg)	Reference
1	[P14,6,6,6] [TCB]	12.6	14	90.35	108.16	[49]
2	[TOAMNaph]	0.95	7.65	97.943	1884.63	[52]
3	TDAMCH	0.75	6.5	96.338	2382.76	[52]
4	HMIMNTf2	0.56	0.92	76.004	2674.27	[52]
5	Cyphos 104	0.56	16.8	98.838	2917.14	[52]
6	OmimPF6	0.809	1.321	48.066	1167.25	[51]
7	Bmim PF6	0.724	2.4	42.43	1179.48	[51]
8	[bmPIP][NTf2]	4.4	28	86.91	267.91	[54]
9	[COC2mPIP] [NTf2]	36.9	9.7	72.02	81.16	[54]
10	[COC2mPYR] [NTf2]	36	2	96.84	601.02	[54]

From the calculation results in Table IX following conclusions can be drawn:

1. Separation with Cyphos 104 requires the largest amount of IL and also takes a substantial amount of water into the Ionic Liquid phase, in-turn giving the best 1-butanol recovery.
2. [TOAMNaph], TDAMCH, [COC2mPYR] [NTf2], show similar amount of 1-butanol recovery in the range of 95% and above.
3. [COC2mPIP] [NTf2] requires the lowest amount of liquid, but 1-butanol recovery is not attractive.
4. [P14,6,6,6] [TCB] on the other hand requires low amount of ionic liquid and achieves a remarkable recovery of 90.35 %.
5. [COC2mPYR] [NTf2], along with [COC2mPIP] [NTf2] and [P14, 6, 6, 6] [TCB] show significant amount of 1-butanol concentration in the IL phase.

Thus, selection of any Ionic Liquid is performed cumulatively based on of recovery achieved, amount of ionic liquid required and water content in the IL phase. Separation of water and 1-butanol using extraction techniques/ using ionic liquids gives rise to another phase of IL with 1-butanol. To obtain pure 1-butanol, this phase needs to be separated. Generally, pervaporation is used to separate the phases ^[51]. However, due to lower volume and higher mass of the ionic liquids, this separation is feasible and provides better results ^[51]. Finally, [TOAMNaph] seems to be the best choice based on the recovery of 1-butanol from water and is used for comparison in further stages.

Even though ionic liquids enjoy various advantages, the process is ridden with problems. Since water tends to enter the IL-rich phase; further complications can arise in subsequent operations. Ionic liquid at times enters the water-rich phase, and hence recovery of IL becomes a separate arduous task. A separate unit operation, like pervaporation or distillation, has to be employed to recover 1-butanol from the separated ionic liquid. With newer and more efficient ionic liquids, extraction of 1-butanol by ionic liquids is expected to be a cost-effective and energy-

efficient technique for separating 1-butanol from its aqueous mixtures.

VII. SALTING

Liquid-liquid phase splitting using salts, which takes place at atmospheric pressure and moderate temperature, has been explored to overcome the energy-intensive distillation for 1-butanol concentration. The influence of electrolytes and inorganic salts on the behavior of 1-butanol-water mixtures has been frequently investigated ^[55-61]. Dissolved salts in aqueous-organic mixtures would either decrease or increase the solubility of the organic species in water. Salting out is observed when the solubility of organic species in water reduces with increase in salt concentration, resulting in an enlarged heterogeneous region of the ternary mixture and hence a higher degree of immiscibility. Salting out is observed after the addition of a certain amount of salt to the solution. This effect is exploited in the extraction of organic compounds from solutions. A salting-out agent with the merits of cheapness, greenness, and stability takes advantage of its reutilization. Chawong et al analyzed the effects of salting-out mechanism of Na₂SO₄, NH₄Cl, NaCl, and (NH₄)₂SO₄. Na₂SO₄ appeared to be the most effective salt among the three, while NH₄Cl is the least effective. The temperature had no significant effect in the range studied on the Liquid-Liquid Extraction (LLE) behavior of these systems ^[55]. Measuring LLE data for the systems 1-butanol-water-KF and 1-butanol-water-K₂CO₃ at 25 °C, revealed that 1-butanol concentrations in organic phase can reach over 96% and 98% when the concentrations of K₂CO₃ and KF and in the aqueous phase are 52.5% and 50.40% respectively. 1-butanol was not detected in the aqueous phase by gas chromatography, resulting in 100% recovery. Thus, water can be separated efficiently from 1-butanol-water solution by adding K₂CO₃ or KF to the system ^[56]. Li et al. found that KCl has higher salting out efficiency than NaCl, with KBr being the least efficient in water+1-butanol+salt system ^[57]. In the case of NH₄Cl,

it was found that the addition of ammonium chloride not only decreased 1-butanol concentration in the water-rich phase but also water concentration in the organic phase ^[58].

Mentioned in Table X are the salt requirements required to achieve a particular 1-butanol concentration in the organic phase per m³ of the 1-butanol-water solution. The 1-butanol recovery is defined as the ratio

of the amount of 1-butanol in the organic phase to the amount of 1-butanol originally present in the aqueous solution. The tie line data was taken from literature and utilized to perform mass balance calculations and hence evaluate the performance of various salts. The salt requirement to achieve a particular level of separation and recovery was estimated.

Table X: Performance of several salts

Salt	1-butanol Concentration (wt %)	Water concentration (wt %)	Temperature (°C)	1-butanol recovery (%)	Salt requirement (g/kg solution)	Reference
NaNO ₃	90.25	9.34	25	15.15	635.08	[58]
Na ₂ SO ₄	93.54	6.45	30	80.28	331.29	[55]
(NH ₄) ₂ SO ₄	94.63	5.36	30	63.	286.45	[55]
KI	82.04	9.74	25	62.58	1428.96	[59]
NaBr	91.61	6.23	25	81.88	924.55	[59]
KBr	90.2	9.11	25	49.03	655.57	[59]
NaCl	93.26	6.56	30	25.79	318.89	[55]
CaCl ₂	88.5	1.5	25	61.72	544.87	[44]
KCl	90.4	9.45	25	86.76	342.86	[57]
KF	98.23	1.76	25	100	995.44	[56]
K ₂ CO ₃	96.5	3.49	25	100	1082.36	[56]

No general trend was observed in the recovery and concentration of 1-butanol in organic phase for different salts. From Table X it can be seen that salting suffers from low recovery for most of the salts. Potential salts that can be employed are potassium fluoride and potassium carbonate. However, handling of potassium fluoride and potassium carbonate is hazardous and may add to the cost. The regeneration of the salt is another drawback of the process. On account of low concentrations of 1-butanol, high energy requirements in the range of 21.9 MJ/kg 1-butanol ^[60] to 28.5 MJ/kg 1-butanol ^[61] are required to evaporate off the unrecovered organics and water from the salt solution. Although process simplicity of salting operation is enticing, salt selection and handling is an arduous task, thereby challenging the economic tradeoff.

studied in this paper are not industrialized because of their techno-economic barriers. The primary optimization target for the downstream separation units is to achieve the lowest energy requirement possible at the highest possible recovery. Complete process designs with these specifications for the recovery of 1-butanol are scarce. Figure VIII is a graphical representation of calculations performed and literature cited in the above sections.

VIII. CONCLUSION

Despite extensive research and collective efforts towards overcoming limitations of low productivity and concentrations of fermentation, most of the technologies

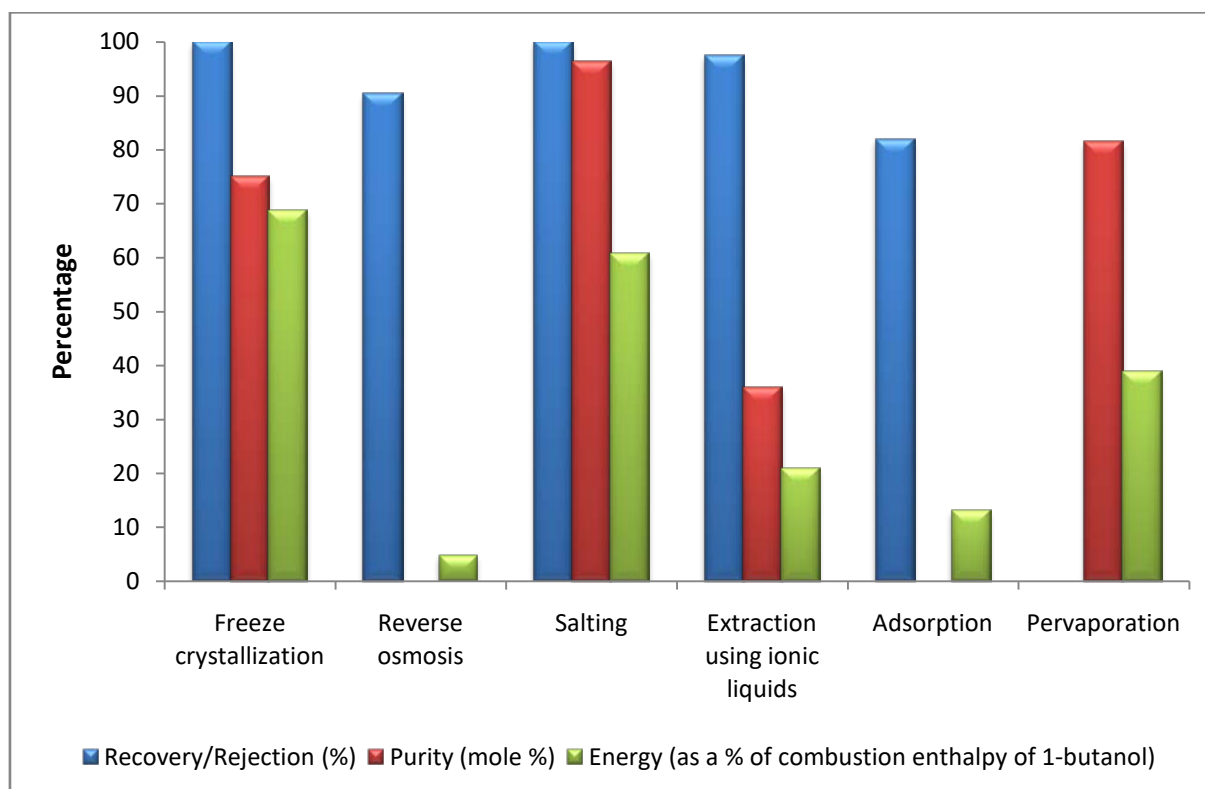


Figure VIII: Comparison of separation processes regarding recovery/rejection, purity and energy requirement

Freeze crystallization and salting provided with high recovery, but the energy associated with these is significant resulting in high operating costs. Besides, salt handling and its recovery are key issues related to salting and it is difficult to maintain sub-zero temperatures and to handle large quantities of ice in case of freeze crystallization. Regarding energy requirement, it is evident that adsorption and reverse osmosis are promising options. ILs are capable of providing high recovery at low energy requirements but need to be followed by a subsequent separation step for IL-1-butanol separation such as pervaporation. To devise an operational process that enjoys high selectivity, nontoxicity and that is energy-extensive, integration of different separation technologies such as pervaporation-distillation, RO-freeze crystallization, IL-pervaporation could be worth trying. Hence, an integrated separation operation to complement their positives and right their drawbacks could be the key. However, all potential options need further proof of industrial long time performance, to obtain additional insights about their operation and performance.

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TABLE OF SYMBOLS

J_A	Flux of component A through the membrane (kmol/s.m ²)
Q_A	Ratio of permeability to membrane thickness for component A (kmol/m.s.Pa)
γ_A	Activity coefficient of component A
P_A^*	Vapor pressure of component A at the given temperature(Pa)
P_2	Permeate Pressure (Pa)
x_A	Mole fraction in feed of component A
y_A	Mole fraction in permeate of component A
R_A	Pressure Ratio for component A
α'	Modified selectivity
B	Separation factor
c_{iP}	Mole fraction of component in permeate
c_{if}	Mole fraction of component in feed
T	Temperature (K)
$D_{AM}/K\delta$	1-Butanol transport parameter (m/s)
ρ	Feed density (kg/m ³)
μ	Feed viscosity (Pa s)
Q	Feed flow rate (m/s)
d_h	Equivalent hydraulic diameter(m)
V_w	Molar volume of pure water (m ³ /kmol)
A	Permeability of pure water (m/s.Pa)
D_{ab}	Diffusivity of butanol in water (m ² /s)
A_t	Effective area tangential to the feed flow (m ²)
π	Osmotic pressure (Pa)
M_w	Molecular weights of water (kg/kmol)
M_b	Molecular weights of 1-butanol (kg/kmol)
C_b	Concentration of 1-butanol (kg/m ³)
Sh	Sherwood number

Re	Reynolds number
Sc	Schmidt number
k_a	Mass transfer coefficient (m/s)
v	Tangential flow velocity (m/s)
C_{a1}	Molar feed 1-butanol concentration (kmol/m ³)
C_{a2}	Molar concentration of 1-butanol on the membrane surface (kmol/m ³)
C_1	Molar density of the feed solution (kmol/m ³)
N_b	Molar flux of water (kmol/s.m ²)
S	Selectivity
D	Distribution coefficient
w_1	Mass fractions of 1-butanol
w_2	Mass fractions of 1-butanol and water
x	Concentration of 1-butanol in solution (kg/m ³)
y	Amount of 1-butanol adsorbed per unit mass of adsorbent

Declarations of interest

None

Funding sources

None

ANNEXURE: CALCULATIONS

REVERSE OSMOSIS

To obtain the rejection of 1-butanol by reverse osmosis, the following calculations were done.

1. To estimate rejection and permeate flux of 1-butanol, the preferential sorption-capillary flow model was employed. The model assumes that all transport takes place through the 'pores' of the membrane skin layer. It defines pore as the space between non-bonded elements in the membrane matrix through which mass transport can occur. It also assumes that solute is rejected at the surface for physicochemical factors and water preferentially gets adsorbed onto the pore walls. The solvent and solute fluxes are,

$$N_A = \frac{D_{AM}}{K\delta} (C_{A2} - C_{A3}) \quad (A1)$$

$$N_B = A(\Delta P - \Delta \pi) \quad (A2)$$

Where, the subscript A refers to 1-butanol and the subscript B refers to water. N_B and N_A are the fluxes of water and 1-butanol through the membrane, respectively. A is the permeability of water through the membrane. $\Delta \pi$ is the osmotic pressure difference across the membrane. ΔP is the pressure difference across the membrane. C_{A2} is the concentration of 1-butanol on the membrane surface at the feed side. C_{A3} is the concentration of 1-butanol on the membrane surface at the permeate side. $D_{AM}/K\delta$ is the 1-butanol transport parameter. A and $D_{AM}/K\delta$ were obtained from literature.

2. To predict the concentration of solute on the membrane surface at the feed side, the film theory was used.

$$C_{A2} = C_{A1} \exp \left(\frac{N_B}{k_g C_1} \right) \quad (A3)$$

Where C_1 is the molar density of the feed solution; k_A is the mass transfer coefficient; and X_{A1} , X_{A2} , and X_{A3} are the mole fractions of the 1-butanol in the feed solution, on the membrane surface at feed side, and in the permeate, respectively. k_A has been calculated using Schock and Miquel's correlation, established for spiral-wound modules and Reynolds numbers in the range of $100 < Re < 1000$.

- The osmotic pressure difference ($\Delta\Pi$) can be estimated from 1-butanol concentration at the two sides of the membrane (C_{A2} and C_{A3}). As the butanol concentration is quite low, the osmotic pressure will be low compared to the pressure difference applied and would be further lower at the permeate side. While calculating osmotic pressure difference, only the osmotic pressure at the feed side of the membrane was considered and that at the permeate side was assumed to be negligible. The osmotic pressure was estimated using the expression.

$$\Pi_A = -\frac{RT}{V_w} \ln \frac{(1000 - C_{A2})/M_B - 2C_{A2}/M_A}{(10000 - C_{A2})/M_B - C_{A2}/M_A} \quad (A4)$$

Hence, solving equations (A2), (A3) and (A4) simultaneously the water flux can be estimated.

Where, T and R are the temperature and the universal gas constant, respectively; M_A and M_B are the molecular weights of 1-butanol and water respectively; V_w is the molar volume of pure water.

- The mole fraction of solute in the permeate can be calculated as

$$X_{A3} = \frac{N_A}{N_A + N_B} \approx \frac{N_A}{N_B} \quad (A5)$$

Equation (A1) has been rewritten in the following form,

$$N_A = \frac{D_{AM}}{K\delta} (C_2 X_{A2} - C_3 X_{A3}) \quad (A6)$$

Where, X_{A2} and X_{A3} are the molar fractions of 1-butanol on the membrane surface and in the permeate, respectively; C_2 and C_3 are the molar densities of the solution on the membrane surface and in the permeate, respectively.

The molar density C_2 was estimated from C_{A2} . The molar density of the permeate (C_3) was assumed to be equal to that of the water.

Hence, from X_{A3} , C_3 , X_{A2} , C_2 , the 1-butanol flux through the membrane can be estimated.

- The rejection of 1-butanol (R) can be estimated from the following expression,

$$R(\%) = \left(1 - \frac{C_{A3}}{C_{A1}}\right) * 100 \quad (A7)$$

PERVAPORATION

Calculations to obtain the output mole fraction of the pervaporation process were carried in the following steps:

- The permeability of the membranes was utilized from the paper of Bai et al. (2015).
- The mole fraction of 1-butanol was evaluated by taking an initial concentration of 20 g 1-butanol in 1000 g solution. This turned out to be 0.004939.
- The temperature of the system for the first stage was taken to be 40 °C, with permeate pressure of around 10 mm Hg.
- Following factors were required to calculate the output mole fraction of the system: Flux equation concerning each component, modified pressure ratio of both the components and the modified selectivity of the system. The following equations were utilized to calculate the flux through the system.

$$J_A = Q_A (\gamma_A * x_A * P_A^* - y_A * P_2) \quad (A8)$$

$$J_B = Q_B (\gamma_B * (1 - x_A) * P_B^* - (1 - y_A) * P_2) \quad (A9)$$

Where J_A is the molar flux across the membrane, Q_A is the ratio of permeability of component through membrane and thickness of membrane, γ_A is the activity coefficient of the component, x_A is the mole fraction of component in the feed, P_A^* is the vapor pressure of the component at the system temperature, y_A is the mole fraction of the component on the permeate side, and P_2 is the pressure on the permeate side. Similar notations of other component named B.

- To calculate the flux, mole fraction of the permeate is required. To estimate the mole fraction, pressure ratios (R_A , R_B) and modified selectivity (α') of the system is required, which is given by:

$$R_A = \frac{P_2}{\gamma_A * P_{A2}^*}; R_B = \frac{P_2}{\gamma_B * P_{B2}^*} \quad (A10)$$

$$\alpha' = \frac{Q_A * \gamma_A * P_A^*}{Q_B * \gamma_B * P_B^*} \quad (A11)$$

- Each value except the activity coefficient is known in the above equation. To calculate the activity coefficient, a code was created in python language which utilized the Soave-Redlich-Kwong model to evaluate the Gibbs free energy of real gas for the particular system. The following set of equations were utilized to estimate the activity coefficient of the system:

$$\varphi_i^L = \frac{G_{iL}^R}{R*T}; \varphi_i^V = \frac{G_{iV}^R}{R*T} \quad (A12)$$

$$\gamma_i = \frac{P * y_i * \varphi_i^V}{x_i * \varphi_i^L * P_i^*} \quad (A13)$$

Where φ_i^L is the fugacity coefficient for liquid phase and φ_i^V is the fugacity coefficient for

gaseous phase, G_{Li}^R is the Gibbs free energy of the component without any ideality in the liquid phase, and G_{Vi}^R is the Gibbs free energy of the component without any ideality in the vapor phase.

- VLE data was taken from Dortmund Data Bank, which was utilized to calculate γ_i values for various inlet mole fractions. This data was then employed to interpolate gamma values for the specific mole fraction of the system. This process was performed for both the components and gamma values of both the components were incorporated.
- Once γ_i were available, both modified pressure ratios and modified selectivity could be calculated. Equations (A8) to (A11) combined to give a quadratic equation explicit in γ_i as follows:

$$a * y_i^2 + b * y_i + c = 0 \quad (A14)$$

Where,

$$a = \alpha' * R_A - R_B$$

$$b = R_B + x - 1 + \alpha' * (R_A + x)$$

$$c = \alpha' * x$$

- This quadratic was solved on excel using goal seek method to find out the mole fraction of the permeate which was then used to find the flux of the particular component through the membrane.
- For the second stage, the output of the first stage was considered as the input of the second stage and similar calculations were performed.

IONIC LIQUID

- Calculations of ionic liquids were performed on the basis of tie-line data obtained from a variety of papers. One such data is shown below:

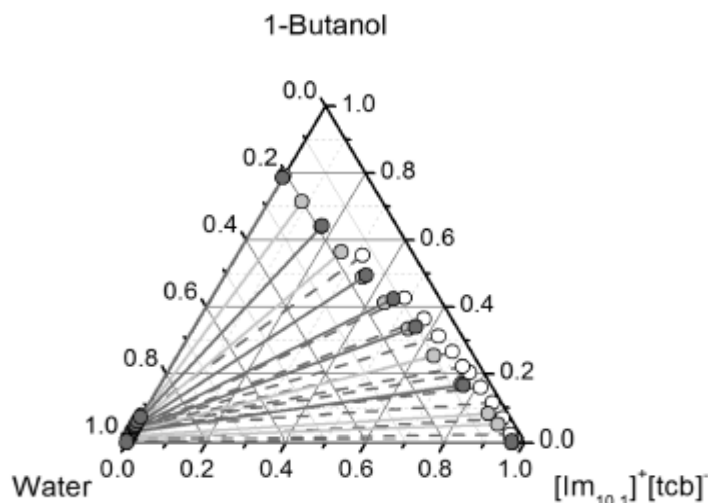


Figure IX: Ternary diagram of 1-butanol-water-ionic liquid system

- The tie line chosen for each of the ionic liquid was the one providing highest selectivity. Based on the tie line, the mole fractions of the components were obtained in each phase. Let, ill denote the amount of ionic liquid in ionic liquid phase, bl denote the amount of 1-butanol in ionic liquid phase, wl denote the amount of water in ionic liquid phase. Similarly, ilw denotes the amount of ionic liquid in the water phase, ww denote the amount of water in the water phase, and bw is the amount of 1-butanol in the water phase.
- So, the mole fraction of ionic liquid and water in ionic liquid phase can be written as:
- Similarly, equations can be written for the water phase. Two more mass balance equations based on the initial concentration of water and 1-butanol can be written as given:

$$980 = wl + bl \quad (A17)$$

$$20 = ww + bw \quad (A18)$$

- Above mentioned six equations were solved simultaneously to obtain the amount of each component in both the phases and amount of ionic liquid required for the separation. Based on the results, the ionic liquids were compared and analyzed.

SALTING

Calculations similar to the one done for ionic liquids were performed for salting to obtain the amount of salt required for different systems and the output composition of each phase.

$$x_{il}^l = \frac{ill}{ill + wl + bl} \quad (A15)$$

$$x_w^l = \frac{wl}{ill + wl + bl} \quad (A16)$$

FREEZE CRYSTALLIZATION

1. The solid-liquid equilibrium data for the binary system of 1-butanol and water was obtained from the paper of Lohmann et al. (1997) which is as follows:

Table XI: Solid-liquid equilibrium data of 1-butanol-water system

X 1-butanol	T (K)
0	273.15
0.55354	269.28
0.59431	267.57
0.64055	264.76
0.69146	260.22
0.75861	251.37
0.80155	241.77
0.8468	227.4
0.87572	212.26
0.89422	199.89

2. The data points between 269.28 K to 199.89 K were regressed to obtain cooling temperature in K (y) as a function of mole fraction of water in the liquid phase (x) with $R^2 = 0.998$

Table XI: Coefficients for estimating specific heat capacity

Compound	A	B	C	D	E
Water	2.76E+05	-2.09E+03	8.125	-1.41E-02	9.37E-06
1-butanol	1.91E+05	-7.30E+02	2.2998	0	0

6. The heat load (Q_1) for cooling the system upto 278.16 was calculated as:

$$Q_2 = \left(\dot{m} \int c_p dT \right)_{\text{water}} + \left(\dot{m} \int c_p dT \right)_{\text{1-butanol}} \quad (\text{A22})$$

7. For further cooling from 278.16 K to 253.53 K, ethanol glycol which was 45 % by weight was used as a coolant. In this case, since the water will start fusing below 273.16 K, the term for latent heat of fusion of ice needs to be accounted for calculating the heat load (Q_2). The latent heat of fusion of ice (L) was taken to be 6017.10 kJ/kmol.

$$Q_2 = \left(\dot{m} \int c_p dT \right)_{\text{water}} + \left(\dot{m} \int c_p dT \right)_{\text{1-butanol}} + \dot{m}_{\text{water}} * L \quad (\text{A23})$$

$$y = 2694x^3 - 2993x^2 + 1160x + 108.5 \quad (\text{A19})$$

3. Using the above function, mole fraction of water in the liquid phase was calculated to be 0.25 at 253.53 K. From this, the mole fraction of 1-butanol in the liquid phase was estimated to be 0.75 using the following equation.

$$x_{\text{1-butanol}} + x_{\text{water}} = 1 \quad (\text{A20})$$

4. The heat load on the system was calculated assuming a feed flow rate of 1000 kg/hr having a concentration of 20 kg/m³ 1-butanol in water at 293.16 K. Hence, flow rate ($\dot{m}$) of 1-butanol in the feed was obtained to be 0.27 kmol/hr and water was 54.40 kmol/hr.
5. Initially, the system was cooled using chilled water upto 278.16 K. The specific heat capacity (c_p) of 1-butanol and water in the feed was taken as a function of temperature (T):

$$c_p = A + BT + CT^2 + DT^3 + ET^4 \quad (\text{A21})$$

Where,

8. The overall heat load(Q) on the system is:

$$Q_1 + Q_2 = Q \quad (\text{A24})$$

ADSORPTION

1. The isotherm equation for adsorption on AC F-400 was obtained by regression of the data available in the paper of Abdegagh et al. (2013). The equation gave a relation between the amount of butanol adsorbed per unit mass of adsorbent (y) and concentration of 1-butanol in the feed solution (x) at equilibrium. The equation is as follows:

$$y_i = \frac{500x_i}{1 + 2130.5x_i} \quad (\text{A25})$$

Where i= 0 or 1; Isotherm equations for other adsorbents were also obtained similarly.

2. Mass balance across a batch adsorption unit was carried out:

$$Lx_o + Sy_o = Lx_1 + Sy_1 \quad (\text{A26})$$

Where, L is the amount of water in the feed (kg); x is the concentration (kg 1-butanol/kg water); S is the amount of adsorbent (kg); y is the amount of 1-butanol adsorbed (kg 1-butanol/kg adsorbent). The subscript 'o' indicates inlet and '1' indicates outlet.

3. Assuming the value of $L=980$ kg; $S=300$ kg; $x_o = 0.02$; $y_o = 0$; and solving equations (A25) and (A26), the value of x_1 and y_1 was determined.