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Assessment of Separation Processes for Recovery of 1-Butanol from its Dilute Aqueous Solution Shreya Akshay Thakkar¹, Atharva Shashank Chikhalikar² and Neha Amol Padwal³ ¹ Institute of Chemical Technology, *Received: 12 December 2018 Accepted: 2 January 2019 Published: 15 January 2019*

7 Abstract

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⁸ Microbial fermentation yields aqueous solutions with concentrations of 1-3

10 Index terms— 1-butanol, aqueous solution, fermentation, separation.

11 **1** Introduction

Author ? ? ?: Department of Chemical Engineering, Institute of Chemical Technology, Mumbai 400019, India. e-mails: shreya.thakkar.13@gmail.com, atharvachikhalikar26@gmail.com, neha.np235@gmail.com 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, ??,3, ??].

1-butanol production on industrial scale occurs via microbial fermentation yielding concentrations of 1-3% by 17 weight. Above concentrations of 2 wt % of 1-butanol, process inhibition occurs, and fermentation is stopped ??4, 18 ??, ??]. Its separation and recovery is a crucial step in the industry. Although distillation is the most widely 19 practiced separation process, its energy requirement is comparable to the energy content of 1-butanol rendering 20 it uneconomical ???, ??]. Much higher fermentation broth concentrations are required to produce an effective 21 liquid-liquid split ??9]. This paper assesses alternative separation methods for 1-butanol recovery such as freeze 22 crystallization, adsorption, pervaporation, reverse osmosis and phase splitting using salts or ionic liquids, and 23 evaluates them on the basis of recovery, purity, and energy-input. 24

We have considered a concentration of 20 kg/m 3 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.

²⁸ **2 II.**

²⁹ 3 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, ??1].

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(D D D D) C

³⁹ 4 Assessment of Separation Processes for

40 Recovery of 1-Butanol from its Dilute Aqueous Solution

41 Abstract-Microbial fermentation yields aqueous solutions with concentrations of 1-3 % by weight of organic 42 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 43 energy-intensive operations such as distillation prove to be uneconomical when compared with the energy content 44 of 1-butanol. Fermentation broth concentrations up to 70 kg/m 3 are required to produce an effective liquid-45 liquid split. The paper aims at assessing several unit operations for recovering 1-butanol from water in terms 46 47 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 48 adsorbents were found to be efficient for extracting 1-butanol from the solution. Multiple stages of pervaporation 49 were capable of providing a high purity stream of 1-butanol. Likewise, freeze crystallization and reverse osmosis 50 also offer feasible alternatives to overcome the separation crisis. The ability of ionic liquids and salts to alter 51 the equilibrium even at low 1-butanol concentrations can be potentially utilized for separation. A comparison of 52 these operations reveals that we need to make a compromise between energy efficiency, recovery, and purity. 53 -butanol has a plethora of uses in the manufacture of commodity as well as specialty chemicals. It possesses 54

numerous advantages as a biofuel. Firstly, it has a higher organic content than ethanol 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]. 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 $R^2 = 0.998$ Using equation (I) and applying lever rule, the variation of 1-butanol concentration in the liquid phase 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 64 water fused to form ice. This temperature is attainable, and there is a significant improvement in 1-butanol 65 concentration from an inlet of 0.005 mole fraction to 0.75 mole fraction in the outlet. More concentrated outlet 66 67 stream can be obtained at lower temperatures. But, it is not feasible to use a cooling agent to attain such low 68 temperatures at an industrial scale. Cooling agents such as liquid nitrogen, solid carbon dioxide or even glycols 69 at very high concentrations can achieve significantly low temperatures but possess handling difficulties. used as a cooling agent at a concentration of 45% by weight. Other cooling agents such as propylene glycol brine can be 70 used, but it has very high viscosity. Calcium chloride can also be used but it is highly corrosive ??14] and has a 71 relatively low specific heat ??15]. 72

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

⁸⁹ 6 III.

90 7 Pervaporation

Pervaporation is a novel membrane technology which has a dual effect of two processes combined in one set-up: 91 namely reverse osmosis and membrane gas separation ??17]. Pervaporation consists of a selective membrane 92 93 through which different entities present in a liquid mixture diffuse according to their permeabilities through 94 the particular membrane ??18]. Thus, the mechanism of separation is the difference in the affinities of the 95 components in the mixture for the specific membrane ??19]. The process is purposefully carried out at a very 96 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, ??8, ??9]. 97 Pervaporation being a membrane-based process, some factors such as permeabilities, flux, separation factors 98 depend upon the type of membrane A recent advance in membrane materials consists of hyper-branched structure 99 to enhance the properties of the membranes like low package density, negligible crystallinity, etc ??24, ??5, ??6] 100 . Bai et al. ??26] developed a highly efficient modification of PDMS membrane which consisted of cross linkers 101

in the form of hyper branched polysiloxane. Due to the novelty of the membrane and performance characteristics 102 depicted, this membrane was utilized for further calculations. C utilized. Separation of 1-butanol and water 103 has been performed by a variety of membranes each with one modification over another to get higher flux 104 and permeate concentrations. According to Vane ??19], poly dimethyl siloxane (PDMS) is a widely used 105 membrane for separation. Vane ??19] effectively tested various PDMS membranes with certain modifications 106 such as integration of membrane with octadecyldiethoxymethylsilane, and PTFE (poly tetra fluoro ethylene) 107 or PP (polypropylene) which were found to have higher separation factor and selectivity than usual PDMS 108 membranes. Liu et al. ??20] performed a separation of water and 1-butanol using ceramic membranes. Li et 109 al. ??21] introduced a new membrane: tri-layer PDMS for effective separation of 1-butanol and water. Wang et 110 al. ??22] took the PDMS one step ahead by generating a zeolite, PDMS matrix membrane for the separation 111 which helps in generating better interface compatibility. Found and Feng ??23] evaluated the properties of PDMS 112 membrane filled with silicalite particularly adapted to separate 1-butanol and water. Year 2019© 2019 Global 113 Journals (DDDD)C 114

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:?? ?? = ?? ?? (?? ?? * ?? ?? * ?? ?? * ?? ?? * ?? 2) (II)

122 $\,$ In a similar manner, we can write equations for the other component.

Where 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 concerning1-butanol mole fraction to obtain activity coefficient at any concentration.

Pressure ratio and modified selectivity has been defined in the following manner: ??18] ?? With the knowledge 128 of permeate pressure (P 2), the initial conditions and the permeabilities, equations (III), (IV) and (V) can be 129 solved simultaneously to obtain the permeate composition of 1-butanol at different stages. The results obtained 130 are stated in Table IV. With the increase in the number of stages from 1 to 2, the output mole fraction of 131 1-butanol increased. Further increase in the number of stages reduces the output concentration but increases 132 the flux as seen in Table IV. The initial increase in the output concentration can be attributed to the rise in the 133 temperature of the feed and high activity coefficient of 1-butanol at the feed concentration, which is not the case 134 for the subsequent stage. 135

The flux of 1-butanol was found to increase along with the process temperature because of the fact that, 136 with an increase in temperature, the saturated pressure of both the components increase while the permeate 137 pressure remains constant. This increases the driving force to which the flux is proportional as shown in 138 Equation (IV). Thus, the flux increases with increase in temperature, even though the permeability decreases. C 139 Pervaporation resulted into permeate mole fraction of about 0.82 at the second stage. Moreover, pervaporation 140 is an environment-friendly alternative which separates the components without affecting microbe activity and 141 growth, which allows for in-situ operation. Thus, pervaporation seems to be a practical alternative for separation 142 of 1-butanol from the water. Kimura et al. have proposed an empirical equation for the estimation of osmotic 143 pressure as a function of 1-butanol concentration ??38]. 144

149 8 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, ??8, ??9].

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, The rejections obtained by cellulose acetate membrane for organic-aqueous solutions are relatively low, especially for low molecular weight organic compounds ??28] 163 . Polyamide membranes have exhibited rejection rates as high as 98% and have a potential application in 164 Ibutanol-water separation **??34**, **??5**].

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 Where, ?? and ?? are the temperature and universal gas constant respectively; ?? is the molar volume of pure water; and ?? ?? and ?? ð ??"ð ??" are the molecular weights of water and 1-butanol, respectively; ?? 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]. transport parameter (D AM /K?) through the membrane. Where ???? is the Schmidt number (??/??D a), ???? is the Reynolds number (d h v??/??), and ??? is the Sherwood number (k a d h /D ab). 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, ?? is the solution viscosity, and ?? is the solution density. molecular size or with solubility parameters ??29, ??1, ??2, ??3].

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Where ?? ??1 is the feed 1-butanol concentration; ?? ??2 is the concentration of 1-butanol on the membrane surface; ?? ?? is the molar flux of water; ?? 1 is the molar density of the feed solution.

The flux of water and 1-butanol through the membrane were then estimated using preferential sorptioncapillary flow model and hence the solute rejection. Solute rejection, water flux as well as the solute flux increased with the applied pressure. 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.

188 **11** V.

Adsorption 1-butanol separation from aqueous solutions and its recovery by adsorption is an energy efficient method with promising results ???]. 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 ???, ??1, ??2].

Abdegagh et al. ???] found that Activated carbon(AC) F-400 was the most effective adsorbent amongst 194 the adsorbents: ZSM-5, AC F-600, NaY, Silicalite, and multi-walled carbon nanotubes studied by them. Their 195 study on the kinetics of adsorbents indicated that AC F-400 and AC F-600 had the fastest adsorption kinetics 196 197 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 198 alumina. Raganati et al. ??42] observed that adsorption capacity of 1-butanol on Amberlite XAD4, Amberlite 199 XAD7, and Zeolite Y increased with temperature and maximum adsorption capacity was found at 318.16 K when 200 temperatures were varied from 298.16 K to 318.16 K. 1-Butanol Rejection (%) 201

²⁰² 12 Pressure difference (MPa)

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.

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. # 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] AC F-400 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.

²¹⁷ 13 Conditions mentioned in

The Table VII allows us to conclude that AC F-400 has the highest adsorption capacity for 1butanol 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 pseudosecond 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 224 et al. experimentally evaluated the recovery of 1-butanol on desorption on AC F-400. According to their study, 225 it is possible to recover 84% of the total 1-butanol adsorbed via thermal desorption process. ??43]. AC F-400 is 226 227 a suitable adsorbent for 1butanol separation of water since it possesses high It is seen from Figure VII that the 228 1-butanol concentration in the rejected stream drastically drops with the increase in mass of adsorbent. Hence, 229 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, 230 the operating cost ??43]. The increased amount of adsorbent required would also increase the capital cost. 231 Hence, a compromise is required between cost and recovery while deciding the operating conditions. 232

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 1butanol 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 insitu 237 separation of fermentation broth resulting from ABE fermentation with an energy demand of about 10% of 238 1butanol combustion enthalpy ??46]. Many studies have evaluated the selectivity of adsorption of 1-butanol 239 and its recovery from the fermentation broth using suitable adsorbents ???, ??3] .Use of adsorption for in-situ 240 recovery of 1-butanol may improve the economics of the fermentation process ??47]. Hence, adsorption is 241 an efficient separation method for this separation. Lack of literature on desorption has held back the use of 242 adsorption-desorption process on the industrial scale for separation of 1-butanol. Liquid-Liquid Extraction using 243 Ionic Liquids 244

1. Toxic nature of the extractant. 2. High selectivity (1-butanol).

3. Loss of liquid to the aqueous phase.

Liquid-Liquid extraction is seen as a potential alternative to energy-intensive techniques for 1-butanolwater 247 separation such as distillation ??48]. However, conventional liquid-liquid equilibrium techniques utilizing organic 248 solvents as extractive phase, suffer from the fact that, separation is not high enough for concentration as low 249 as obtained from the fermentation broth ??9]. Moreover, organic liquids used as extractants such as tert-amyl 250 ether, diisopropyl ether, and dibutyl ether result in significant damage and contamination ??49] . Hence, the 251 focus has now shifted from organic liquids to ionic liquids for extraction of 1-butanol from the water. Ionic liquids 252 are the ones made up entirely of ions. The term ionic liquid is different from ionic solution as in; NaCl with 253 water forms an ionic solution, while molten NaCl is ionic liquid ??50]. Ionic liquids are advantageous due to 254 various factors such as low vapor pressure, and high thermal and chemical stability ??48]. Ionic liquids make 255 way for enormous possible cation-anion combinations which can be utilized to prepare task-specific ionic liquids 256 (ILs). However, following concerns should be addressed before selecting an ionic liquid ??9] : Year 2019© 2019 257 Global Journals (DDDD)C 258

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. ?? = ?? 1 ???? * ?? 2 ???? ?? 1 ???? * ?? 2 ???? (IX) ?? = ?? 1 ???? ?? 1 ???? (X)

Various ionic liquids have emerged in the field of separation, and this paper attempts to review and evaluate 262 some of them based on their potential for separation. Nann et al. ??48], Domaska et al. ??49], Davis et 263 al. ??9], Fadeev et al. ??51], Garcia-Chevez ??52], Ha et al. ??53], came up with various ionic liquids 264 for the separation of water from 1-butanol. Some of them are listed in Table VIII along with their distribution 265 coefficients and selectivity. Distribution coefficient and selectivity are defined as: The tie lines and the extraction 266 data of both the phases specified in the papers were utilized to perform mass balance calculations and evaluate 267 the performance of most of the ionic liquids. The tie lines were selected such that they offered the maximum 268 selectivity as well as recovery of 1-butanol. Table IX gives details of the same.1-octyl-3-methyl-1H- imidazol-3-ium 269 hexafluoro Phosphate [omim][PF 6] (D D D D) C 11 1-hexyl-270

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. show similar amount of 1-butanol recovery in the range of 95% and above.

$_{274}$ 14 [COC2mPIP]

275 [NTf2] requires the lowest amount of liquid, but 1-butanol recovery is not attractive.

$_{276}$ 15 [COC2mPYR] [NTf2], along with [COC2mPIP]

277 [NTf2] and [P14, 6, 6, 6] [TCB] show significant amount of 1-butanol concentration in the IL phase.

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.

²⁹⁰ 16 VII.

²⁹¹ 17 Salting

Liquid?liquid phase splitting using salts, which takes place at atmospheric pressure and moderate temperature, 292 has been explored to overcome the energy-intensive distillation for 1-butanol concentration. The influence of 293 electrolytes and inorganic salts on the behavior of 1-butanol-water mixtures has been frequently investigated 294 [55][56][57][58][59][60][61]. Dissolved salts in aqueous-organic mixtures would either decrease or increase the 295 solubility of the organic species in water. Salting out is observed when the solubility of organic species in water 296 reduces with increase in salt concentration, resulting in an enlarged heterogeneous region of the ternary mixture 297 and hence a higher degree of immiscibility. Salting out is observed after the addition of a certain amount of salt to 298 the solution. This effect is exploited in the extraction of organic compounds from solutions. A salting-out agent 299 with the merits of cheapness, greenness, and stability takes advantage of its reutilization. Chawong et al analyzed 300 the effects of salting-out mechanism of Na 2 SO 4, NH 4 Cl, NaCl, and (NH 4) 2 SO 4. Na 2 SO 4 appeared to be 301 the most effective salt among the three, while NH 4 Cl is the least effective. The temperature had no significant 302 effect in the range studied on the Liquid-Liquid Extraction (LLE) behavior of these systems [55]. Measuring 303 LLE data for the systems 1-butanol-water-KF and 1-butanol-water-K 2 CO 3 at 25 o C, revealed that 1butanol 304 concentrations in organic phase can reach over 96% and 98% when the concentrations of K 2 CO 3 and KF and 305 in the aqueous phase are 52.5% and 50.40% respectively. 1-butanol was not detected in the aqueous phase by 306 gas chromatography, resulting in 100% recovery. Thus, water can be separated efficiently from 1-butanol-water 307 solution by adding K 2 CO 3 or KF to the system [56]. Li et al. found that KCl has higher salting out efficiency 308 than NaCl, with KBr being the least efficient in water+1-butanol+salt system [57]. In the case of NH 4 Cl, Year 309 2019 Thus, selection of any Ionic Liquid is performed it was found that the addition of ammonium chloride not 310 only decreased 1-butanol concentration in the water-rich phase but also water concentration in the organic phase 311 [58]. Mentioned in Table X are the salt requirements required to achieve a particular 1-butanol concentration in 312 the organic phase per m 3 of the 1-butanol-water solution. The 1-butanol recovery is defined as the ratio of the 313 amount of 1-butanol in the organic phase to the amount of 1-butanol originally present in the aqueous solution. 314 315 The tie line data was taken from literature and utilized to perform mass balance calculations and hence evaluate 316 the performance of various salts. The salt requirement to achieve a particular level of separation and recovery was estimated. VIII. 317

318 18 Conclusion

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

324 **19** C

325 No general trend was observed in the recovery and concentration of 1-butanol in organic phase for different salts. 326 From Table X it can be seen that salting suffers from low recovery for most of the salts. Potential salts that 327 can be employed are potassium fluoride and potassium carbonate. However, handling of potassium fluoride and 328 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/kg329 1-butanol [60] to 28.5 MJ/kg 1-butanol [61] are required to evaporate off the unrecovered organics and water 330 from the salt solution. Although process simplicity of salting operation is enticing, salt selection and handling 331 is an arduous task, thereby challenging the economic tradeoff. Freeze crystallization and salting provided with 332 high recovery, but the energy associated with these is significant resulting in high operating costs. Besides, salt 333

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, ILpervaporation 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.

344 20 References Références Referencias

345 21 Annexure: Calculations

346 22 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,?? ?? = ?? ???? ???? (?? ??? ???) (A1) ?? ?? = ??(??? ? ???) (A2)

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. 4. The mole fraction of solute in the permeate can be calculated as?? ??3 = ?? ?? ?? ?? ??? ????????? ???(A5)

Equation (A1) has been rewritten in the following form,?? ?? = ?????? ????? (?? 2 ?? ?? 2 ?? ?? 3 ?? ??3) (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. 5. The rejection of 1-butanol (R) can be estimated from the following expression, ??(%) = ?1 ? ?? ??3 ?? ??1 ? * 100(A7)

375 23 Pervaporation

Calculations to obtain the output mole fraction of the pervaporation process were carried in the following steps:1. The permeability of the membranes was utilized from the paper of Bai et al. (2015).

3. The temperature of the system for the first stage was taken to be 40 0 C, with permeate pressure of around 10 mm Hg. 4. 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.

382 ?? ?? = ?? ?? (?? ?? * ?? ?? * ?? ?? * ?? ?? * ?? ?? * ?? 2) (A8)?? ?? = ?? ?? (?? ?? * (1 ? ?? ??) * ?? ?? * ?? ?? * ?? ?? * ?? 2) (A9)

384 Where ?? ?? is the molar flux across the membrane, ?? ?? is the ratio of permeability of component through 385 membrane and thickness of membrane, ?? ?? is the activity coefficient of the component, ?? ?? is the mole fraction of component in the feed, ?? ?? * is the vapor pressure of the component at the system temperature, 386 ?? ?? is the mole fraction of the component on the permeate side, and ?? 2 is the pressure on the permeate 387 side. Similar notations of other component named B. 5. To calculate the flux, mole fraction of the permeate is 388 required. To estimate the mole fraction, pressure ratios (?? ?? , ?? ??) and modified selectivity (? ?) of the 389 system is required, which is given by: C 2. The mole fraction of 1-butanol was evaluated by taking an initial 390 concentration of 20 g 1-butanol in 1000 g solution. This turned out to be 0.004939.?? ?? = ?? 2 ?? ?? 391

gaseous phase, ?? ???? ?? is the Gibbs free energy of the component without any ideality in the liquid phase, and ?? ???? ?? is the Gibbs free energy of the component without any ideality in the vapor phase. 7. VLE data was taken from Dortmund Data Bank, which was utilized to calculate ?? ?? 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. 8. Once ?? ?? were available, both modified pressure ratios and modified selectivity could be calculated. Equations (A8) to (A11) combined to give a quadratic equation explicit in ?? ?? as follows:

399 ?? * ?? ?? 2 + ?? * ???? + ?? = 0 (A14)

404 24 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:

2. The tie line chosen for each of the ionic liquid was the one providing highest selectivity. Based on the 407 tie line, the mole fractions of the components were obtained in each phase. Let, ill denote the amount of ionic 408 liquid in ionic liquid phase, bl denote the amount of 1-butanol in ionic liquid phase, wl denote the amount of 409 water in jonic liquid phase. Similarly, ilw denotes the amount of jonic liquid in the water phase, www denote the 410 amount of water in the water phase, and by is the amount of 1-butanol in the water phase. 7. For further cooling 411 from 278.16 K to 253.53 K, ethanol glycol which was 45 % by weight was used as a coolant. In this case, since 412 the water will start fusing below 273.16 K, the term for latent heat of fusion of ice needs to be accounted for 413 calculating the heat load (Q2). The latent heat of fusion of ice (L) was taken to be 6017.10 kJ/kmol. 8. The 414

overall heat load(Q) on the system is: ???? ?? + ???? ?? = ???? 1 + ???? 1 (A26)





415

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Figure 2: Figure



Figure 3:

V

Figure 4: Figure V :



Figure 5:

Figure 6: Figure VI :



Figure 7: Figure VII :



Figure 8:

Figure 9:



Figure 10: Figure VIII :

Figure 11: ©

Figure 12:



Figure 13: 3 .©Figure IX :

Ι

Feed flow rate (1-butanol+water) Feed concentration

Feed temperature Under the conditions mentioned in Table $1000~{\rm kg/hr}$ 20 kg/m 3 1-but anol in water 293.16 K

Figure 14: Table I :

\mathbf{II}

Cooling	Concentration	Specific	Viscosity	vxE1000gy	required	Liquid	phase	e 1-
temper-	by $\%$ weight of	heat	$(Pa \ s)$	to co	ol 1000	butanol		mole
ature (K) upto 264	ethylene glycol	capacity (kJ/kg K)		kg/hour (MJ/ho	r feed ur)	fraction crystalliz	in ation	after

Figure 15: Table II :

III

	Assessment of Separation Processes for R	lecovery of	'1-Butanol	from its Dilute Aqueous Se
Year 2019 12		-		-
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sue				
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neering				
Global	Parameter Temperature (K)	Stage I	Stage II	Stage
		313.16	318.16	III
				363.16
	1-butanol Permeability $(mol.m/(m 2 $	8.88*10	8.04*10	4.69*10
	.s.Pa)	-11	-11	-11
	Water Permeability $(mol.m/(m 2 .s.Pa))$	1.34^*10	$1.34^{*}10$	$1.34^{*}10$
		-11	-11	-11
	Permeate Pressure (Pa)	1333.22	1333.22	133.22

Figure 16: Table III :

Figure 17:

\mathbf{IV}

			?? ????
		?? =	1?????????(V)
			????
			1????????
Figure IV: Plot of permeate 1-butanol mole fra	ction versus	s Stage num	ber
Parameter	Stage I	Stage II	Stage III
Temperature (K)	313.16	318.16	363.16
Permeate Mole Fraction of 1-but anol (y b)	0.21	0.81	0.81
Permeate Flux of 1-butanol $(kg/m 2 s)$	$0.017^{*}10$	$0.45^{*}10$ -	1.6*10 -3
	-3	3	
Permeate Flux of water $(kg/m 2 s)$	0.016*10	0.025*10	0.21*10 -3
	-3	-3	

Figure 18: Table IV :

 \mathbf{V}

[Note: © 2019 Global Journals]

Figure 19: Table V :

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?)	1.91*10 -6 m/s	Molar volume of pure water (V w)	18.07 m 3 /kmol
Feed density (?)	1000 kg/m 3	Permeability of pure water (A)	7.83*10 -12 m 3 /s m 2 Pa
Feed viscosity (??)	$0.001 \mathrm{Pa} \mathrm{s}$	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

Figure 20:

\mathbf{VI}

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	balance equations and the adsorp-
	tion isotherm
adsorption model by simultaneously solving the	equations. Table VII depicts the
material	results.
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Figure 21: Table VI :

\mathbf{VII}

Adsorbent	Temperature (K)	Isotherm equation *	Concentration of 1-butanol in rejected stream (kg/m 3)
ZSM-5 with 4%	Room tempera-	$y = 0.079 x \ 0.082 \ \#$	4.48
alumina	ture		
Amberlite	318.16	y=57.12x/(1+0.21x) [42]	1.37
XAD4			
Amberlite	318.16	y=152.2x/(1+0.2x) [42]	0.46
XAD7			
Zeolite Y	318.16	y=43.92x/(1+0.18x) [42]	1.79
	Room tempera-	y=500x/(1+2130.5x) ##	0.18
	ture	••• • • • •	

[Note: * y represents amount of 1-butanol adsorbed per unit mass of adsorbent and x represents concentration of 1-butanol in solution]

Figure 22: Table VII :

VIII

Sr. No	Ionic Liquid	Feed Concen- tration (%wt 1-butanol)	Temper (K)	r æle ret	i Dis tribut re- spect to 1- butanol Coef- ficient with	t i&n ferences
1	I-decyl-3- methylimidazolium tetracyanoborate [Im 10.1] + [tcb] ? 4-decyl-4-	<10	308.16	85	8	[48]
2	methylmorpholinium tetracyanoborate [Mo 10.1] + [tcb] ? 1-decyl-3- methylimidazolium	<10	308.16	78	6	[48]
3	bis(trifluoromethyl sulfonyl)imide [Im 10.1] + [ntf2] ? 4-decyl-4-methyl morpholinium	<10	308.16	70	7.9	[48]
4	bis(trifluoromethylsulfonyl)- imide [Mo 10.1] + [ntf2] ? trihexyltetradecylphosphoni	<10	308.16	73	6.1	[48]
5	um tetracyanoborate [P14,6,6,6][TCB] 1-decyl-3-	-	308.16	50- 903	25-65	[49]
6	methylimidazolium tetracyanoborate	-	308.16	45- 125	28-48	[49]
7	[DMM][TCB] 1-butyl-3-methylimidazolium bis(trifluoromethyl [bmim][Tf2N] sulfonyl)imide	Higher than fer- mentation obtained in ABE	298.16	10- 100	1.4-7.3	[9]
8	1-hexyl-3-methylimidazolium bis(trifluoromethyl [hmim][Tf2N] sulfonyl)imide	Higher than fer- mentation obtained in ABE	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		2.01	296.16	55.37	0.923	[51]

Figure 23: Table VIII :

 \mathbf{IX}

Sr. No	Ionic Liquid	1- butanol Con- cen- tration in IL phase	Water Con- cen- tration in IL phase (wt %)	1- butanol Re- covery (%)	Ionic Liquid *1000 (kg) Require- ment	Reference
1	[P14,6,6,6]	(wt %) 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	2]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],

Figure 24: Table IX :

Х

Salt	1-butanol Concentra-	Water con- centration $(-+)^{(7)}$	Tempera (o C)	at luba itanol recovery	Salt requirement (g/kg solution)	Reference
	%)	(Wt %)		(%)		
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	94.63	5.36	30	63.	286.45	[55]
SO 4						
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]

Figure 25: Table X :

\mathbf{of}

	J A Q A	Flux of component A through the membrane (kmol/s.m 2) Ratio of permeability to membrane thickness for component A	
	<u></u>	(kmol/m.s.Pa)	
		Activity coefficient of component A	
	PA*	Vapor pressure of component A at the given temperature(Pa)	
	P 2	Permeate Pressure (Pa)	
	хАуА	Mole fraction in feed of component A Mole fraction in permeate of component A	Year 2019
	R A	Pressure Ratio for component A	
	?? ?	Modified selectivity	
	?	Separation factor	
	c iP	Mole fraction of component in permeate	
	c if	Mole fraction of component in feed	
	Т	Temperature (K)	
	D AM /K?	1-Butanol transport parameter (m/s)	
	? '	Feed density (kg/m3)	
D	??	Feed viscosity (Pa s)	
D			
D			
D			
)			
Ć			
(
`	Q	Feed flow rate (m/s)	
	d h	Equivalent hydraulic diameter(m)	
	V w	Molar volume of pure water (m 3 /kmol)	
	А	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)	
	??	Osmotic pressure (Pa)	
	M w	Molecular weights of water (kg/kmol)	
	Mb	Molecular weights of 1-butanol (kg/kmol)	
	Cb	Concentration of 1-butanol (kg/m 3)	
	Sh	Sherwood number	
		© 2019 Global Journals	

Figure 26: Table of Symbols

XI

I Version x 1-butanol 0 0.55354 0.59431 0.64055 0.69146 0.75861 0.80155 0.8468 0.87572 0.89422 2. ?? = I 30 Year 2019 Volume XIX Issue 2.76E + 05(DDDD Water 2.09E + 03) Journal of Researches in Engineering Global

?? 2 = ????? ?? ?? ??????

(A23) 1????????????????

+ ????? ????????? * ??

[Note: ?????????+ ?????? ?? ?? ????CFreeze Crystallization 1]

Figure 27: Table XI :

XI

D D D D) C (© 2019 Global Journals

Figure 28: Table XI :

416 .1 Declarations of interest None

⁴¹⁷.2 Funding sources None

Where, the subscript A refers to 1-butanol and the subscript B refers to water. N B and N A are the fluxes of 418 water and 1-butanol through the membrane, respectively. A is the permeability of water through the membrane. 419 ?? is the osmotic pressure difference across the membrane. ?P is the pressure difference across the membrane. 420 C A2 is the concentration 1-butanol on the membrane surface at the feed side. C A3 is the concentration of 421 1-butanol on the membrane surface at the permeate side. D AM /K? is the 1-butanol transport parameter. A 422 and D AM /K? were obtained from literature. 2. To predict the concentration of solute on the membrane surface 423 at the feed side, the film theory was used. 424 Where C 1 is the molar density of the feed solution; k A is the mass transfer coefficient; and X A1 , X A2 425

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.

429 4. Similarly, equations can be written for the water phase. Two more mass balance equations based on the 430 initial concentration of water and 1-butanol can be written as given:

431 5. Above mentioned six equations were solved simultaneously to obtain the amount of each component in both 432 the phases and amount of ionic liquid required for the separation. Based on the results, the ionic liquids were 433 compared and analyzed.

434 .3 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.

- 437 [?? ?? = 0; and solving equations (A25) and (A26), the value of ?? 1 and ?? 1 was determined] ?? ?? = 0.02.
- 438 ?? ?? = 0; and solving equations (A25) and (A26), the value of ?? 1 and ?? 1 was determined,
- (?? is the amount of 1-butanol adsorbed (kg 1-butanol/kg adsorbent). The subscript 'o' indicates inlet and '1' indicates outlet]
 (?? is the amount of 1-butanol adsorbed (kg 1-butanol/kg adsorbent). The subscript 'o' indicates inlet and '1' indicates outlet.
- 442 [?? is the concentration (kg 1-butanol/kg water] ?? is the concentration (kg 1-butanol/kg water,
- 443 [Assuming the value of L=980 kg] Assuming the value of L=980 kg, (S=300 kg)
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