Capturing renewable isobutanol from model vapor mixtures using an all-silica beta zeolite

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ABSTRACT

Isobutanol is a promising renewable platform chemical, produced via fermentation. In the conventional downstream processing, isobutanol is recovered from the fermentation broth via evaporation or gas-stripping, followed by purification via distillation. Alternatively, an adsorptive separation can be used to recover isobutanol from the generated vapor mixture, however this has remained unexplored in the literature. In this work, we investigate the use of a hydrophobic all-silica beta zeolite (Si-BEA) to recover isobutanol from model vapor mixtures via adsorption. The Si-BEA zeolite shows a high selectivity for isobutanol over water (α = 35) and ethanol (α = 10) and excellent mass transfer properties under dynamic conditions. Sharp isobutanol breakthrough profiles were obtained, leading to a fraction of unused bed of only 6% at a gas residence time of only 0.6 s. The adsorbed isobutanol could be fully desorbed via thermal regeneration and an isothermal purge allows to remove co-adsorbed ethanol and water. The results of this work thus show the promising properties of Si-BEA for the recovery of renewable isobutanol from vapor mixtures.

1. Introduction

Bio-alcohols, such as bioethanol and biobutanol, are important platform chemicals [1–4] which can be produced from renewable feedstocks via fermentation [5–12]. While the production of bioethanol [5–7] and bio-n-butanol [8–12] is already performed for many decades, the fermentative production of renewable isobutanol has been only recently established [13–15]. Being a branched molecule, the renewable production of isobutanol opens new routes towards important chemical feedstocks such as isobutylene and xylene isomers [16].

A major challenge in the fermentative production of bio-alcohols is the recovery of the alcohol from the fermentation broth, which is usually present in low concentrations due to product inhibition (<2 wt% for isobutanol) [17–21]. This makes the conventional recovery and purification via distillation economically [22] and energetically demanding [23,24]. The use of in-situ product recovery techniques [25–27], allows to simultaneously recover the produced alcohol while relieving product inhibition. Based on patent literature, the industrial production of isobutanol involves in-situ product recovery via the use of a liquid extractant [20,28], gas-stripping [20] or a flash evaporation step, using a vacuum and heating of the fermentation broth to generate a vapor mixture containing isobutanol [21]. After gas-stripping or flash evaporation, the isobutanol present in the vapor mixture is completely recovered and purified via distillation [20,21].

Alternatively, an isobutanol-selective adsorbent can be used to capture the produced isobutanol from the obtained vapor mixture. Such an approach has been previously investigated in the context of fermentative n-butanol [29–36], ethanol [36,37] and 2-butanol recovery [38,39], but has remained unexplored in the context of isobutanol fermentation. Vacuum stripping combined with 2-butanol adsorption on silicalite-1 was modelled by Pereira et al. [38,39] The modelled stripping vapor contained 20 wt% 2-butanol, 52 wt% water and 28 wt% CO₂. Hence, a large amount of water is still present in the vapor mixture. Using hydrophobic silicalite-1 as adsorbent, they were able to obtain a high concentration of 2-butanol (>98 wt%) via thermal swing adsorption. Since this concentration is much higher than the azeotropic composition of the 2-butanol/water mixture (72.5 wt%), the energy demand of the subsequent complete purification via distillation halved from 36 MW to 17 MW [38]. In our recent work, we investigated the use of an all-silica LTA zeolite (ITQ-29) for n-butanol recovery from model vapor mixtures.
A complex channel-type pore structure consisting of straight channels recovery of renewable isobutanol from vapor mixtures. Zeolite beta has [40]. We characterized the in-house synthesized zeolite via the measurement of Ar, water and alcohol vapor isotherms. The selectivity of the adsorbent for isobutanol over water was calculated from the pure component isotherms using the Ideal Adsorbed Solution Theory (IAST) and compared with some selected commercial adsorbents. The isobutanol/water and isobutanol/ethanol selectivity of Si-BEA was also investigated experimentally via breakthrough experiments. Finally, the effect of gas velocity on the separation and thermal regeneration of the material was explored.

2. Materials and methods

2.1. Adsorbates, gases and commercial adsorbents

An overview of the used alcohol adsorbates and gases, with their respective purity and supplier, was added in Supporting Information (Tables S1 and S2). Besides the self-synthesized all-silica beta zeolite (vide infra), three commercial adsorbents (high silica beta zeolite CP811C-300, activated carbon F300 and Optipore L-493) were used in this study. The suppliers and details of these materials can be found in Supporting Information (Table S3). Images of the employed adsorbents are added in Supporting Information (Fig. S3), including the zeolite powder and binder-free pellets used for breakthrough experiments.

2.2. All-silica zeolite beta synthesis

All-silica beta zeolite was synthesized according to the previously published method [41], from a gel of molar composition SiO$_2$: 0.54 TEAOH: 0.54 HF: 7.5 H$_2$O. The gel was prepared by hydrolysis of tetraethylorthosilicate in an aqueous solution of tetraethylammonium hydroxide (TEAOH) and the mixture was stirred at room temperature to allow the evaporation of ethanol. To this solution, HF was added together with a suspension containing nanocrystalline dealuminated zeolite Beta seeds [42] in water to promote the formation of smaller crystallites. The mixture was transferred to Teflon-lined stainless-steel autoclaves and heated to 140 °C while being rotated at 60 rpm. After 5 days, the autoclaves were quenched, and the content filtered and washed with deionized water. Finally, the zeolite was calcined at 580 °C for 3 h in static air. Samples were characterized via powder x-ray diffraction (XRD), scanning electron microscope images (SEM) and $^{29}$Si solid-state nuclear magnetic resonance (SS-NMR). The results indicated the successful, defect-free synthesis of zeolite beta crystals (Figs. S3–S5).

2.3. Ar isotherms & pore size distribution

Ar isotherms were measured using the volumetric method on an Autosorb AS-1 (Quantachrome). The corresponding pore size distribution was determined using a NLDFT kernel for silica, assuming cylindrical pores.

2.4. Vapor isotherms

Alcohol and water vapor isotherms were measured using a gravimetric system (SGA-100H, VTI Corporation). The system uses nitrogen as a carrier gas, which is bubbled through a cooled or heated evaporator to generate vapors at a varying partial pressure. The generated vapors can be diluted with extra carrier gas and the temperature of the sample is controlled by an oven. The all-silica beta, CP811C-300 and activated carbon F300 samples were activated in-situ, prior to the measurement of the isotherm, under a constant nitrogen flow (200 Nml/min) by heating at 1 °C/min to 350 °C and holding the final activation temperature constant for 2 h. For the Optipore L-493 resin, the same program, but with a maximum temperature of 120 °C was used. In these experiments, a sample mass between 5 and 10 mg was used.

2.5. Stripping gas composition

In order to obtain a model of the composition of the stripping gas, used to remove isobutanol from the fermentation broth, we modelled the fermenter as a flash tank in Aspen®. A liquid stream, with a composition corresponding to an isobutanol fermentation broth, was fed together with a stripping gas stream (CO$_2$). The composition of the outgoing liquid and vapor streams were calculated using the Wilson activity coefficient model, and a total pressure of 1 bar and temperature of 30 °C was assumed. A feed stream of 1 kg/h liquid fermentation broth with a feed gas stream of 1.7 kg CO$_2$/kg isobutanol was used, which is a ratio liquid/gas feed encountered in the similar acetone-butanol-ethanol fermentation process [12]. The composition of the model liquid feed and corresponding vapor pressures in the stripping gas are shown in Table S5.

2.6. IAST calculations

To allow comparison of the selectivity of the Si-BEA zeolite for isobutanol over water with some selected commercial, hydrophobic adsorbents we calculated the amount of isobutanol and water adsorbed from the pure component isotherms on these materials using the Ideal Adsorbed Solution Theory (IAST), originally developed by Myers & Prausnitz [43]. IAST assumes the adsorbent to be thermodynamically inert and the surface accessible for adsorption is assumed to be temperature-invariant and the same for all adsorbate molecules [43]. A detailed overview of the governing equations and the solution approach we followed, is presented in Supporting Information (Section S6).

2.7. Breakthrough experiments

Breakthrough experiments with binary and ternary vapor mixtures (in the presence of an inert carrier gas) were carried out on an in-house build setup, as in our previous work [30,33,44]. A scheme of this setup, detailed experimental conditions, adsorbent regeneration procedure and packing procedure for the column can be found in Supporting Information (Section S4). From the obtained concentration profiles at the column outlet, the amount adsorbed of each component (Eq. S1) and the selectivity for isobutanol could be calculated (Eq. S3). The effect of the gas velocity on the isobutanol breakthrough profiles was assessed by calculating the fraction of unused bed (FUB) for isobutanol (Eq. S5).

3. Results and discussion

3.1. Single component isotherms

The pore volume and pore size distribution of the all-silica beta (Si-BEA) sample was analyzed via the measurement of Ar isotherms at –186 °C (Fig. 1A and B). The peak in the pore size distribution...
corresponds to a pore diameter of 1 nm, which is slightly larger than the theoretical pore-openings of the linear (0.57 × 0.75 nm) and tortuous channels (0.56 × 0.65 nm) of zeolite beta [40]. The micropore volume based on the Ar isotherm and calculated via NLDFT is 0.23 cc/g, corresponding well to typical micropore volumes reported in the literature, based on $N_2$ or Ar adsorption [24,45,46]. Only a very small hysteresis loop was observed (Fig. 1A), indicating an almost complete absence of mesopores in the synthesized sample.

Vapor isotherms of different alcohol molecules and water were measured to investigate the affinity and capacity of the all-silica beta zeolite (Si-BEA) for these probe molecules (Fig. 1C and D). First, only a very small amount of water (maximum of 0.01 g/g) was observed to adsorb (Fig. 1C and D). In all-silica zeolites, the uptake of water is often highly increased by the presence of silanol defects in the material, in spite of their theoretical hydrophobic nature [47–52]. The low amount of water adsorbed is thus indicative of the low amount of these defects present, as also confirmed by the absence of $Q^3$ resonances in the $^{29}$Si MAS NMR spectrum due to Si(3Si,1OH) species (see Fig. S5). Secondly, for the linear and branched-chained alcohols investigated (Fig. 1D), a much higher saturation capacity was observed (0.15–0.16 g/g), compared to water. The saturation capacities correspond well to those found in the literature on high-silica (commercial) beta zeolites for the adsorption of alcohols from dilute aqueous mixture [24,46,53] or determined via molecular simulations [54]. For the smaller alcohols (e. g. methanol and ethanol) a clear sigmoidal Type V isotherm was observed (Fig. 1C and D). Such a sigmoidal isotherm is typical for polar molecules adsorbing in hydrophobic pores and has been reported for the adsorption of alcohol vapors or water on activated carbons [55–60], all-silica zeolites [30,31,47,48,50,61–65] and hydrophobic metal organic frameworks [66–68]. With increasing aliphatic chain length of the alcohol molecule, the inflection point in the isotherm becomes less pronounced (Fig. 1C) and for $n$-butanol and isobutanol, a Type I isotherm was observed.

### 3.2. Comparison with commercial adsorbents

The theoretical performance of the Si-BEA adsorbent was compared with some representative commercial materials for the separation of isobutanol from fermentation mixtures [69]. From a flash calculation in Aspen (Table S5), the composition of the vapor mixture after gas stripping was estimated. Besides isobutanol (373 Pa), a small amount of ethanol is present in the stripping gas (82 Pa) and water is present in much larger amounts (4113 Pa). Thus, isobutanol and water vapor isotherms were measured (Fig. 2) and the IAST was used to predict the isobutanol/water selectivity (Table 1).

First, the isotherms of Si-BEA are compared to those of CP811C-300, which is a commercial beta zeolite with a high Si/Al ratio of 300 (Table S3). As can be observed in Fig. 2A, the isobutanol isotherms of both materials are very similar, having a Type I shape and comparable saturation loading (0.16 g/g). Although the micropore volume of the commercial sample is slightly lower (0.17 cc/g – Table S3) than the Si-BEA material (0.23 cc/g), some mesopores were found to be present in the CP811C-300 sample (Fig. S2), which can clarify why the total loading of isobutanol on Si-BEA and CP811C-300 are similar. The presence of mesopores in the CP811C-300 sample can also explain the less-steep saturation plateau in the isobutanol adsorption isotherm (Fig. 2). On the other hand, the water isotherm on both materials is quite different (Fig. 2B). While the equilibrium capacity of water on the Si-BEA sample never exceeds 0.01 g/g, the water isotherm on CP811C-300 is almost linear and at the water vapor pressure of the mixture, around 0.14 g/g of water is adsorbed. Hence, although the Si/Al ratio of this material is quite high, a strong competition between water and isobutanol can be expected. This is reflected in the binary isobutanol/water selectivity as predicted by IAST (Table 1), which is high for the Si-BEA zeolite ($\alpha = 72$) and much lower for the commercial material ($\alpha = 3$).

In a recent study, we identified activated carbon (F300) and the hydrophobic polymeric resin Optipore L-493 as selective and promising adsorbents for the recovery of isobutanol directly from the liquid fermentation broth [69]. The isobutanol isotherm on the activated...
carbon has a type I shape, while the isobutanol isotherm on L-493 has a type IV shape with a small initial step (Fig. 2). For both adsorbents, the amount of isobutanol adsorbed is almost unaffected by the water vapor present in the mixture, leading to a maximal isobutanol/water selectivity of 53 for the investigated binary mixtures (Fig. 3D). Similarly, for the ternary vapor mixtures, the amount of co-adsorbing water is low (\(<0.03\) g/g) and the isobutanol/water selectivity varies between 22 and 35 (Fig. 3F). These results thus highlight the hydrophobicity of the Si-BEA material, as also visible from the pure component water isotherms (Fig. 1D). This hydrophobicity leads to the preferential adsorption of isobutanol over water for both binary and ternary model vapor mixtures.

Secondly, isobutanol is also preferentially adsorbed over ethanol for both the binary and ternary mixtures investigated (Fig. 3). Ethanol is adsorbed and subsequently displaced by isobutanol, leading to ‘roll-up’ of the ethanol concentration profile (Fig. 3B and C). During the breakthrough of ethanol, isobutanol was observed to elute as a very sharp front (Fig. 3). In all cases, the isobutanol concentration at the outlet of the column reaches the feed value in less than \(\approx 1.5\) min, which was the maximal resolution which could be obtained via the analysis with gas chromatography. The type I isotherm shape of isobutanol (Fig. 1), will lead to self-sharpening of the isobutanol mass transfer zone when the concentration profile propagates through the column during a dynamic breakthrough experiment. However, the final broadness of the breakthrough profile will be a balance between these self-sharpening and kinetic effects, such as heat & mass transfer and axial dispersion, which will be flow rate depended [70]. To investigate the influence of these effects on the shape of the isobutanol breakthrough profile, we performed breakthrough experiments and varied the interstitial gas velocity (Fig. 4A). At the employed gas velocities (Fig. 4A), the residence time of the carrier gas in the column is 2.6 s, 1.3 s and 0.6 s.

The concentration profile of isobutanol is largely independent of the gas velocity (Fig. 4A). Only slight broadening of the isobutanol profile is observed at the highest gas velocity. Fig. 4B shows the FUB (Eq. S5) as a function of the gas velocity, giving a measure for how efficient a packed adsorbent bed is used when the adsorption step is stopped before complete breakthrough [70]. Due to the very sharp isobutanol front, the column bed is used to almost maximal efficiency, with only 3–6% of the bed not completely saturated. Only a minor increase of the FUB with gas
Fig. 3. Binary isobutanol (240 Pa)/water (3900 Pa) (A), isobutanol (240 Pa)/ethanol (270 Pa) (B) and ternary isobutanol (300 Pa)/ethanol (1200 Pa)/water (3900 Pa) (C) breakthrough profiles measured at 40 °C and a total flow rate of 21.3 Nml/min. The adsorbed amounts and isobutanol selectivity for binary (D & E) and ternary (F) mixtures with a fixed partial pressure of isobutanol (240 Pa – D & E, 300 Pa – F) and a varying water (D) or ethanol partial pressure are also shown (E & F). Water vapor pressure in (F) was equal to 3900 Pa. Corresponding breakthrough profiles are shown in (A–C) and Supporting Information (Fig. S6–S8), adsorbed amounts can be found in Tables S13–S15.

Fig. 4. (A) Ternary isobutanol (300 Pa)/ethanol (300 Pa)/water (3900 Pa) breakthrough profiles at 40 °C with a varying interstitial gas velocity: 0.04, 0.08 and 0.16 m/s. The experimental time is normalized by the average breakthrough time of isobutanol, adsorbed amounts are shown in Table S16. (B) The FUB (Eq. S5) for isobutanol for the experiments shown in (A). (C) Breakthrough profiles of acetone (190 Pa), n-butanol (300 Pa), ethanol (50 Pa) and water (4200 Pa) on a packed ITQ-29 column at 40 °C with a gas velocity of 0.03 m/s [30].
velocity was observed (Fig.4B), thus indicating that no large mass transfer resistances, dispersion or heat effects are present under the conditions studied. While in an industrial application, the zeolite would be formulated with a binder, which could influence mass and heat transfer effects, these first results appear promising.

To give a comparison, breakthrough profiles of a model acetone-n-butanol-ethanol (ABE) mixture are shown in Fig.4C for the all-silica LTA zeolite (ITQ-29), which we studied previously for the recovery of renewable n-butanol from vapor mixtures [30]. The breakthrough experiment was carried out on a similar column as for Si-BEA (length, internal diameter, zeolite pellet size) and corresponds to a gas residence time of 4 s. On this system, the n-butanol isotherm has a type I shape, the ethanol isotherm is sigmoidal, acetone is excluded from the pores and water adsorbs only in trace amounts [30]. Hence, it shares similarities with the Si-BEA zeolite, where the isobutanol isotherm has a type I shape, the ethanol isotherm is sigmoidal and water adsorbs in small amounts (vide supra). However, on ITQ-29, a relative broad n-butanol breakthrough profile is observed (Fig.4C), compared to the isobutanol profile on Si-BEA (Fig.4A), while the experiments were carried out a lower gas velocity than on the SI-BEA column. The FUB for n-butanol is around 65%, which is a large difference compared to the FUB of isobutanol on Si-BEA (Fig.4C). This difference could be related to kinetics, since the pore opening of ITQ-29 (0.42 nm) is much smaller than that of Si-BEA (0.57 × 0.75 nm). However, the difference could also be related to the difference in affinity (e.g. steepness of the isotherm) of both materials for n-butanol and isobutanol respectively. A more detailed study, investigating mass transfer kinetics, would be needed to elucidate these differences. Still, this first comparison with ITQ-29 highlights the efficiency with which the Si-BEA adsorbent bed is used for the recovery of isobutanol.

3.4. Thermal regeneration

After saturation of the adsorbent, the adsorbed isobutanol will have to be desorbed from the column, which can for instance be done by employing a thermal swing. In this work, after each adsorption breakthrough experiment, the packed SI-BEA column was regenerated by purging at fixed temperature (40 °C) with carrier gas for 30 min, followed by controlled external heating of the column at 1 °C/min to 350 °C, using a convection oven. The recorded concentration profiles for the thermal desorption after saturation of the column with a binary isobutanol/ethanol and ternary isobutanol/ethanol/water vapor mixture are shown in Fig.5. The concentration profile of ethanol decreases rapidly, and no ethanol was detected at the column outlet after 10 min. (Fig.5A). Hence, the small amount of co-adsorbed ethanol could be desorbed by isothermal purging of the column. The isobutanol concentration at the outlet is also observed to decrease during the isothermal purge. When the external heating of the column starts, the isobutanol concentration at the column outlet increases again, until it reaches 2 times the feed concentration after 105 min (corresponding to an external temperature of 120 °C). Subsequently, a sharp decrease in the outlet concentration is observed and after 130 min, no isobutanol is detected at the column outlet. A similar desorption profile for ethanol and isobutanol is observed for the ternary mixture (Fig.5B), while water desorbs faster than ethanol and is undetectable after 4 min. Due to the smaller sensitivity of the TCD for organic components, the isothermal part of the desorption profile of isobutanol (between 0 and 30 min), visible in Fig.5A, is not visible in Fig.5B. Still, from both desorption profiles, it can be concluded that after 10 min, only pure isobutanol desorbs from the column. The isothermal purge thus allows to desorb the side components (ethanol and water) co-adsorbed on the column, while only a small amount of isobutanol is desorbing at a low concentration. The subsequent heating allows to fully recover the adsorbed isobutanol. A more detailed experimental and/or modelling approach could allow to optimize the isothermal purge step and heating rate of the column, to obtain an optimal isobutanol purity and recovery.

Fig. 5. Thermal regeneration profiles of the Si-BEA column after saturation with a binary isobutanol (240 Pa)/ethanol (270 Pa) mixture (A) and a ternary isobutanol (300 Pa)/ethanol (320 Pa) and water (3900 Pa) (B) at 40 °C. Regeneration was carried out using a carrier gas flow rate of 23.6 Nml/min and the recorded temperature profile in the column oven is also shown on the graph. Profile (A) was measured using the FID detector, profile (B) using the TCD detector of the GC (see Supporting Information).

4. Conclusion

We investigated the use of an all-silica beta zeolite for the recovery of renewable isobutanol from fermentation vapor mixtures. Due to its superb hydrophobicity, the Si-BEA zeolite shows a high selectivity for isobutanol over the typical mixture side components (ethanol and water). Furthermore, the Si-BEA zeolite showed remarkable mass transfer properties as observed from the sharp isobutanol breakthrough profiles under high gas velocities, leading to an efficient use of the adsorbent bed. The adsorbed isobutanol could be recovered via an increase in temperature, while an isothermal purge allows to desorb co-adsorbed ethanol and water. The results of this work thus show the promising properties of all-silica beta for the recovery of renewable isobutanol from vapor mixtures. Future work should focus on the detailed modelling and experimental study of a thermal swing process, allowing a detailed economical and energetical comparison with the conventional distillation process.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References


