Supplementary Information

Range analysis to determine the most significant parameters for the butanol dehydration

In this work, the range analysis of the results achieved according to the orthogonal array design (OAD) was done in the same way as that in the references. [1-3] First, the average values of each of the butanol dehydration indices at equilibrium including water uptake, butanol uptake, water selectivity, butanol recovery, and maximum effluent butanol concentration at level 1 and 2 of the operation parameters were determined and denoted as k_1 and k_2, respectively. The subscripts of k represent level 1 and 2 of each parameter. The operating parameters investigated in this work included temperature (A), pressure (B); feed butanol concentration (C), feed butanol-water liquid flow rate (D) and particle size (E).

For example, to determine the effect of temperature on water uptake, the average water uptake obtained at level 1 temperature, i.e. 95°C for all runs designed by the OAD method in this work was calculated and noted as k_1, and that at level 2 temperature 111^{o}C was calculated and noted as k_2. Same treatment was done for all parameters and dehydration performance indices. Table S1 summarizes the respective results.

Secondly, the Range Value, denoted by Δ, was determined by the difference in the maximum and minimum k values obtained for each factor and each performance index.[1-3] Specifically, in this work there are only two levels for each factor, Δ is thus determined as follows:

$$\Delta = |k_1 - k_2| \qquad (1)$$

Ranking was then done in the order of the highest to the lowest values of Δ for each performance index. The parameter having the highest rank (i.e. 1) in respect to the highest range value Δ is the most significant parameter on the respective index of dehydration performance, while the lowest rank (i.e. 5) has the least effect.[2-4]

Table S1. Results of Range analysis

Mean values	A	B	C	D	E
Water Uptake					
Mean values	A	B	C	D	E
k_1	0.15	0.18	0.26	0.13	0.19
k_2	0.01	0.03	0.03	0.10	0.07
Δ	0.14	0.15	0.23	0.03	0.12
Rank	3	2	1	5	4
Butanol uptake					
Mean values	A	B	C	D	E
k_1	0.29	0.13	0.17	0.14	0.27
k_2	0.18	0.34	0.35	0.32	0.22
Δ	0.11	0.21	0.18	0.18	0.05
Rank	3	1	2	2	4
Water selectivity					
Mean values	A	B	C	D	E
k_1	1.61	2.25	2.14	1.39	1.59
k_2	1.89	1.25	1.36	2.11	1.91
Δ	0.28	1	0.78	0.72	0.32
Rank	5	1	2	3	4
Butanol recovery					
Mean values	A	B	C	D	E
k_1	40.96	74.60	64.72	46.47	54.51
k_2	68.52	34.89	44.77	69.02	54.98
Δ	27.56	39.71	19.95	16.55	0.47
Rank	2	1	3	4	5
Maximum effluent butanol concentration					
Mean values	A	B	C	D	E
k_1	95.96	98.53	97.24	95.2	96.50
k_2	97.70	95.13	96.58	98.6	97.16
Δ	1.74	3.4	0.66	3.4	0.66
Rank	2	1	3	1	3

A Temperature (°C); **B** Pressure (kPa); **C** Feed butanol Conc. (v %) **D** Feed butanol-water liquid flow rate (mL/min); **E** Particle size (mm)

As per the range analysis of water uptake shown in Table S1, the feed butanol concentration (C) having the highest Δ value indicated that it was the most significant influencing factor for the water uptake. At the level 1 of the butanol feed concentration being 55 v/v%, the average water uptake represented by $k_{1,\ \text{water uptake}}$ was 0.26 g g-ads-1; while at level 2, 95 v/v% butanol, water uptake ($k_{2,\ \text{water uptake}}$) was significantly decreased to 0.03 g g-ads^{-1}. For water uptake, pressure and temperature had the most influence after feed butanol concentration. Feed liquid flow rate and particle size in the tested ranges had less effects on water uptake.

In regard to butanol uptake, pressure was found to be the most significant parameter affecting it, followed by feed butanol concentration, temperature, feed liquid flowrate and particle size. Butanol uptake was found to be increased from 0.13 g $g\text{-}ads^{-1}$ to 0.34 g $g\text{-}ads^{-1}$ when the pressure increased from 135 to 201 kPa. As lesser butanol uptake was preferred in the present study with a selective water adsorption approach, lower pressure of 135 kPa was found to be favorable over a higher pressure of 201 kPa. Butanol feed concentration and feed liquid flow rate were observed to have a similar effect on butanol uptake and they collectively were ranked as the second most important factors. For a preferential lower butanol uptake, lower values of the above two parameters were found to be favorable. With the third significant factor being the temperature, it was seen that as temperature was increased from 95 to 111°C, butanol uptake decreased from 0.29 g $g\text{-}ads^{-1}$ to 0.18 g $g\text{-}ads^{-1}$, which indicated the exothermic nature of butanol adsorption. It was reported [5] that with increasing temperature at constant pressure and vapor feed concentration, ethanol uptake decreases rapidly compared to water uptake. In addition, the solubility of a substance determines its chemical potential, which in turn controls adsorption. When the solubility of the adsorbate increases with increasing temperature, adsorption is decreased and vice versa. In most cases, physical adsorption decreases with increasing temperature [6] and the same pattern was observed in the present study. Particle size in the tested range was observed to have the least influence on butanol uptake.

Water selectivity is a very critical process performance criterion in adsorption, as it translates to the preferred adsorptive species over the undesired.[7] The higher the water selectivity, the better the performance of dehydration process. Pressure was found to be the most crucial factor affecting water selectivity (Table S1). Lower pressure of 135 kPa resulted in a higher water selectivity of 2.25. Butanol feed concentration was the next significant influencing factor for selectivity. At a lower butanol feed concentration of 55 v/v%, a higher water selectivity of 2.14 was obtained. Chang et al. also observed that with increased ethanol feed concentration, water adsorption selectivity by cornmeal decreased. [5] Feed liquid flow rate was seen to be the third important factor and at a higher feed flow rate of 3 mL min^{-1}, a higher selectivity of 2.11 was obtained. Particle size and temperature did not seem to have significant impact on selectivity under the tested range of conditions. Vareli et al. studied the adsorption of water and ethanol on wheat straw with two different ranges of particle sizes - 80–100 and 100–120 mesh and observed similar water selectivity (water separation factors) obtained at the two ranges of particle sizes.[8] Maximizing butanol recovery is one of the primary targets in selective water adsorption process. As per the range analysis in Table S1, it was found that pressure was the most significant factor affecting butanol recovery. At a lower pressure of 135 kPa, a higher butanol recovery of about 75% was obtained compared to only 35% recovery at 201 kPa. In order to obtain a high butanol recovery, a lower pressure is preferred. The second most influential factor was temperature followed by feed butanol concentration, and feed liquid flow rate. At a higher bed operation temperature, lower feed butanol concentration, and higher liquid feed flow rate, a relatively high butanol recovery was obtained. Chang et al. have also stated that productivity (recovery) increases with increased ethanol concentration, but start to decrease at higher ethanol concentrations because of increased resistance to diffusion of water through ethanol.[5] The particle size within the tested range was again found to have an insignificant role on butanol recovery.

The primary purpose of a selective water adsorption process is to obtain high purity butanol as a direct end product from a low titer butanol. Pressure and feed liquid flow rate were found to have the most significant influence on the maximum effluent butanol concentration (Table S1). A lower pressure of 135 kPa and a higher feed flow rate of 3 mL min^{-1} resulted in 98.4 v/v % butanol concentration from as low as 55 v/v % butanol concentration (Table S1). Temperature was the second most influential factor but the resultant butanol concentration at the tested temperatures were only slightly different from each other; being 95% and 98% recovery at 95°C and 111°C, respectively. Butanol feed concentration and particle size also had least effects on this index.

References

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