

MFI zeolite as adsorbent for selective recovery of hydrocarbons from ABE fermentation broths

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Abstract 1-Butanol and butyric acid are two interesting compounds that may be produced by acetone, butanol, and ethanol fermentation using e.g. *Clostridium acetobutylicum*. The main drawback, restricting the commercialization potential of this process, is the toxicity of butanol for the cell culture resulting in low concentrations of this compound in the broth. To make this process economically viable, an efficient recovery process has to be developed. In this work, a hydrophobic MFI type zeolite with high silica to alumina ratio was evaluated as adsorbent for the recovery of butanol and butyric acid from model solutions. Dual component adsorption experiments revealed that both butanol and butyric acid showed a high affinity for the hydrophobic MFI zeolite when adsorbed from aqueous model solutions. Multicomponent adsorption experiments using model solutions, mimicking real fermentation broths, revealed that the adsorbent was very selective to the target compounds. Further, the adsorption of butyric and acetic acid was found to be pH dependent with high adsorption below, and low adsorption above, the respective pKa values of the acids. Thermal desorption of butanol from MFI type zeolite was also studied and a suitable desorption temperature was identified.

Keywords Butanol · Adsorption · Zeolites · Langmuir · Butyric acid · MFI

List of symbols

Variables

ABE	Acetone, Butanol and Ethanol
C	Concentration
V	Volume
b	Langmuir adsorption parameter (L/g)
q _{max}	Saturation loading (g/g)

Subscripts

<i>i</i>	Adsorbate specie <i>i</i>
<i>e</i>	Equilibrium

1 Introduction

Energy demands of the world are ever increasing in this industrial era. With the depleting reservoirs of fossil fuel, the need for new, sustainable fuels and chemicals is more urgent than ever. In the future, biofuels will likely emerge as one of the key replacements of fossil fuels in the transportation market. To replace gasoline and diesel used, biofuels with approximately the same physical and chemical properties are desired. 1-butanol (or simply butanol) produced from renewable resources is a very promising fuel in this sense. For instance, butanol has higher energy density than ethanol, and it is also less polar than ethanol diminishing the problem of water dissolving in the fuel (Durre 1998). Butanol is also an important industrial chemical, which can be used as solvent for paints, dyes, coating, varnishes etc. It is also a precursor or intermediate for chemical synthesis of many plastics and chemicals e.g. hydraulic fluids and safety glass (Jin et al. 2011). Currently, butyric acid is produced industrially by chemical synthesis, by the oxidation of butyraldehyde obtained from crude oil derived propylene (Cascone 2008). It is an important

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additive used in the food industry and has various applications in animal feed supplements due to its ability to reduce bacterial colonization (Immerseel et al. 2005). Butyric acid can also be further derived into a number of commercial interesting compounds, for example cellulose acetate butyrate, butyl acetate, 4-heptanone and butanol.

Butanol can be produced by acetone, butanol and ethanol (ABE) fermentation using *Clostridium acetobutylicum* or *C. beijerinckii* microorganisms, which at the same time are producing acetone and ethanol. However, due to the toxicity of butanol, the maximum concentration of butanol in the broth is limited to ca. 20 g/L in this process with a relative composition of ABE of ca. 3:6:1 (Oudshoorn et al. 2009a). Due to this toxicity of butanol to the cell culture, it is highly desirable to recover butanol from the fermentation broth whilst performing the fermentation to reduce butanol inhibition and increase substrate yield. In addition, by continuously removing the butanol from fermentation broth the productivity of the overall fermentation process can be increased. Recovery of butanol by ordinary distillation is very energy demanding, thus more efficient processes are desired. Adsorption is an efficient separation technique, which has been suggested as a feasible method to recover 1-butanol from fermentation broths (Garcia et al. 2011; Oudshoorn et al. 2009a, 2009b; Milestone and Bibby 1981; Qureshi et al. 2005; Maddox 1982; Saravanan et al. 2010; Woods 1995). In particular, adsorption on hydrophobic adsorbents, such as silicalite-1, was recently identified as a promising means of recovering 1-butanol from fermentation broth as compared to liquid–liquid extraction and pervaporation (Ezeji et al. 2004, 2007; Qureshi et al. 2005; Oudshoorn et al. 2009b). Butyric acid is a precursor to butanol, which is produced during the acidogenic phase of the ABE fermentation. At a critical pH and acid concentration the fermentation enters the second part called the solventogenic phase where butyric acid is converted to butanol. The acidogenic phase can be prolonged by maintaining a neutral pH and hence producing butyric acid via ABE fermentation may be an interesting option under some circumstances. Therefore, efficient alternatives for recovering butyric acid from fermentation broths should also be developed.

Although a reasonable amount of data can be found in the literature regarding butanol recovery from ABE fermentation broths using adsorbents (Ezeji et al. 2004, 2007; Qureshi et al. 2005; Milestone and Bibby 1981, 1983; Meagher et al. 1998), relatively few investigations report quantitative information, e.g. Langmuir adsorption parameters, that may be used as input for modeling the performance of adsorption columns (Oudshoorn et al. 2009a; Saravanan et al. 2010). High silica MFI adsorbents in general show high selectivity towards butanol, but breakthrough experiments show that the adsorption is

rather slow. In contrast, relatively little has been reported on butyric acid recovery. To the best of our knowledge, only Oudshoorn et al. (2009a) reported limited data on the adsorption of butyric acid on MFI type zeolite. At the conditions studied, butyric acid was reported to adsorb even stronger than butanol on the zeolite.

In this paper, results from batch adsorption experiments using high silica ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 230$) MFI zeolite as adsorbent are reported. Both dual component adsorption experiments, i.e. adsorption from mixture of one hydrocarbon and water, as well as multicomponent adsorption experiments, i.e. adsorption from mixtures of several hydrocarbons in water, were carried out. Adsorption isotherms of butanol, ethanol, acetone, butyric and acetic acid at room temperature were determined. Extended Langmuir adsorption isotherms were fitted to the dual component data. The adsorption of butyric- and acetic acid was carried out at pH values above and below the pK_a values of the acids to elucidate the effect of speciation of the acid on the adsorption. Moreover, adsorption from model fermentation mixtures was carried out to determine the adsorption selectivities in multicomponent adsorption experiments.

2 Materials and method

2.1 Materials

A commercial MFI zeolite powder (AkzoNobel) with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 230 in sodium form was used as adsorbent. The surface area of the adsorbent is 403 m²/g. Butanol (99 %), ethanol (99 %) and sodium chloride (99 %) used in the experiments were purchased from Sigma chemicals. Butyric acid (99 %) was purchased from Alpha Aesar. Acetic acid (100 %) and acetone (99.9 %) were obtained from Merck Chemicals. Sodium hydroxide (99.9 %) from Merck chemicals was used to regulate the pH of the solutions. All solutions were prepared from MilliQ-water.

2.2 Experimental methods

Prior to the adsorption experiments, the zeolite adsorbent was calcined in air at 500 °C for 4 h in order to desorb any adsorbed molecules. Liquid phase adsorption equilibrium experiments were performed in closed stirred glass Erlenmeyer flasks of 50 mL. Solutions were prepared by adding appropriate amounts of adsorbates to water; in addition sodium chloride at a concentration of 10 mM was used as background electrolyte. Approximately 40 mL of solution and 1 g adsorbent was then added to the flasks. The solutions were allowed to equilibrate with the dispersed adsorbent for 48 h on a shaking table. Thereafter, the

zeolite powder was separated from the solution via centrifugation at 10,000 rpm for 15 min. The supernatants were filtered using the 0.2 µm syringe filter and the concentrations of the adsorbates were determined by high pressure liquid chromatography (HPLC) and RI detection, using a Perkin-Elmer series 200 instrument equipped with a 125-0115 (BioRad) column in hydrogen form and 0.005 M H₂SO₄ in water was used as mobile phase at a flow rate of 0.6 mL/min.

The zeolite powder was recovered and one sample was used for determining the desorption properties by thermogravimetric analysis coupled with mass spectroscopy (TG-MS) using a Netzsch STA 409 Thermo gravimetric instrument equipped with a quadrupole mass spectrometer. The sample was heated at a rate of 5 °C/min and argon at a flow rate of 100 mL/min was used to carry the released vapors to the mass spectrometer.

To determine the loading of the adsorbate in the zeolite, a mass balance equation was used:

$$q_i = \frac{(C_{i,0} - C_i) \cdot V_o}{m_{z,0}} \quad (1)$$

where q_i is the mass of adsorbate per unit mass of adsorbent, $C_{i,0}$ is the initial concentration of adsorbate in the solution, C_i is the concentration of the adsorbate in the solution at equilibrium, V_o is the volume of solution brought in contact with adsorbent, $m_{z,0}$ is the initial mass of the adsorbent.

The experimentally determined isotherms were then fitted to the Langmuir adsorption model.

$$q_i = \frac{q_{\max} b C}{1 + b C} \quad (2)$$

where q_{\max} is the saturation loading and b is the Langmuir adsorption parameter.

3 Results

3.1 Single component adsorption from aqueous solutions

Figure 1 shows the adsorption isotherms of butanol, acetone and ethanol adsorbed from binary hydrocarbon/water solutions in the zeolite at room temperature. All adsorbates adsorb in the zeolite and the shapes of the isotherms are typical for adsorption in microporous materials. Among the adsorbates, butanol shows the highest affinity for the zeolite followed by acetone and ethanol. This trend is expected and may be rationalized in terms of the relative hydrophobicity of the adsorbates and the hydrophobic character of the adsorbent. Moreover, it may be seen that the Langmuir model fits the experimental data well for all

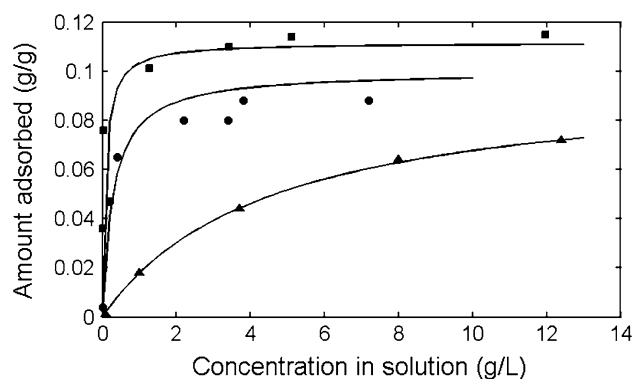


Fig. 1 Experimental adsorption isotherms at room temperature for acetone (black circle), butanol (black square) and ethanol (black up-pointing triangle) on MFI. Full lines represent the Langmuir model fitted to experimental data

Table 1 Langmuir parameters for butanol, ethanol, acetone, butyric and acetic acid from this work and from previous reports

Adsorbate	b (L/g)	q_{\max} (g/g)	References
Butanol	12.4	0.12	This work
	42.8	0.118	Oudshoorn et al. (2009a, b)
	0.191	0.0854	Saravanan et al. (2010)
Ethanol	0.23	0.098	This work
	0.34	0.093	Oudshoorn et al. (2009a, b)
		0.12	Bowen and Vane (2006)
Acetone	3.47	0.10	This work
	1.65	0.121	Oudshoorn et al. (2009a, b)
Butyric acid (pH 4)	5.7	0.13	This work
Butyric acid (pH 6)	139	0.130	Oudshoorn et al. (2009a, b)
	1.40	0.025	This work
Acetic acid (pH 4)	0.28	0.14	This work
		0.09	Bowen and Vane (2006)

three compounds. The fitted saturation loadings (q_{\max}) and the Langmuir adsorption parameters (b) are listed in Table 1. First of all, the saturation loadings obtained in the present work are in close agreement with previous reports. The Langmuir adsorption parameters previously reported scatters significantly; however the values obtained in this work are within range of previously reported values (Oudshoorn et al. 2009a, b; Saravanan et al. 2010).

Butyric acid and acetic acid are precursors which are produced before ABE during the ABE fermentation. As butyric acid and acetic acid is produced, there is a drop of the pH in the fermenter. Butyric acid may in some cases be considered as a product and the recovery of butyric acid from the fermentation broth is therefore of interest. Moreover, if there is any butyric acid left in the broth when recovering the butanol, the presence of butyric acid may cause a problem by competing with butanol for adsorption in

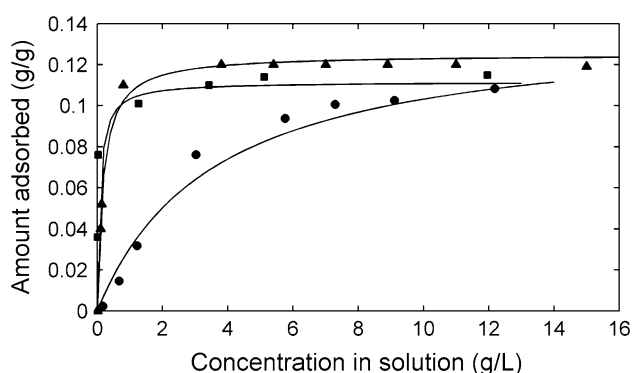


Fig. 2 Experimental adsorption isotherms at room temperature for acetic acid (black circle), butanol (black square) and butyric acid (black up-pointing triangle) on MFI at pH 4. Full lines represent the Langmuir model fitted to experimental data

the zeolite. It has previously been reported that butyric acid showed significantly higher affinity for the MFI zeolite with Langmuir adsorption parameter four times larger for butyric acid than for butanol (Oudshoorn et al. 2009a), however the pH was not specified. Therefore, it is important to study the adsorption behavior also of butyric and acetic acid in both their protonated and deprotonated forms.

Figure 2 shows adsorption isotherms for butyric-, acetic acid and butanol adsorbed from binary hydrocarbon/water solutions together with the Langmuir model fitted to the experimental data. Again the Langmuir model fits the experimental data well. The isotherms of butyric and acetic acid were determined at pH 4 i.e. below the pK_a values of the acids, i.e. the acids should predominantly be in the protonated form. The isotherms of butyric acid and butanol are very similar in appearance; both molecules are showing high affinity for the hydrophobic zeolite. On the other hand, acetic acid shows significantly lower affinity towards zeolite as compared to butanol and butyric acid at these conditions as could be expected from its more polar nature. These findings for ABE are in agreement with the findings reported previously by Oudshoorn et al. (2009a), however, the value of the Langmuir adsorption parameter (*b*) for butyric acid determined in this work was lower than that reported by Oudshoorn. These results show that butyric acid also have a high affinity towards MFI zeolite, and therefore an adsorption based process may also be a feasible option for recovering butyric acid from fermentation broths.

Figure 3 shows the adsorption isotherms of butyric acid adsorbed from binary hydrocarbon/water at pH 4 and 6, i.e. below and above the pK_a value of the acid together with Langmuir model fitted to the experimental data. The adsorption isotherm of acetic acid at pH 6 is also shown. There is a clear difference in the adsorption behavior of the protonated and deprotonated form of the acid, with the protonated form showing much higher affinity for the zeolite than the deprotonated one, again this may be

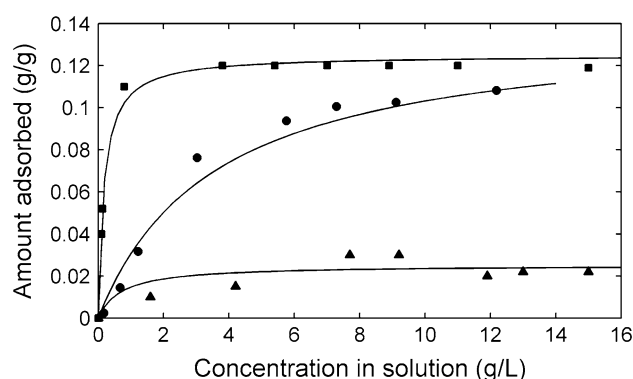


Fig. 3 Experimental adsorption isotherms at room temperature for butyric acid at pH 4 (black square), acetic acid at pH 4 (black circle) and butyric acid at pH 6 (black up-pointing triangle) on MFI zeolite. Full lines represent the Langmuir model fitted to experimental data

Table 2 Measured equilibrium adsorption of model fermentation broths of multicomponent mixtures of acetone, ethanol and butanol in water by MFI at room temperature and near neutral pH

Concentration in solution (g/L)			Adsorbed concentration (g/g)		
Acetone	Ethanol	Butanol	Acetone	Ethanol	Butanol
3.40	1.20	5.17	0.0077	0.0038	0.1
4.30	1.60	7.30	0.04	0.0000	0.11
5.30	1.88	9.20	0.01	0.0008	0.1
6.60	2.34	12	0.01	0.0008	0.11

rationalized in terms of the hydrophobicities of the molecules with deprotonated species being more polar than the protonated species. This is interesting as it shows that the affinity of the butyric- and acetic acids for the zeolite may be controlled by adjusting the pH value of the solution.

For example, it is pivotal that the adsorption of butyric acid in the fermentation broth is minimized if recovery of butanol is the target. At pH 6, the adsorption of acetic acid will be even lower than the other components because of its highly hydrophilic character, so it will most likely not cause any problem during the butanol recovery process. The Langmuir parameters obtained are listed in Table 1.

Oudshoorn et al. (2009a) and Saravanan et al. (2010) previously reported Langmuir parameters in their studies; their values are also included in Table 2 for comparison. Saturated loading (*q*_{max}) values for all the components are in good agreement with the values previously reported.

3.2 Batch adsorption experiments from model fermentation broths

3.2.1 Acetone, butanol and ethanol

To study the competitive adsorption between the main products in an ABE fermentation broth, multicomponent

Table 3 Measured equilibrium adsorption of model fermentation broth of butyric acid and acetic acid on MFI at pH 6

Concentration in solution (g/L)		Adsorbed concentration (g/g)	
Acetic acid	Butyric acid	Acetic acid	Butyric acid
1.5	7.5	0.000	0.020
2.3	10.7	0.000	0.04
9.7	45.1	0.000	0.119

batch adsorption experiments with the same relative concentration of ABE as found in a typical ABE fermentation broth but at different total concentrations were performed at near neutral pH. Table 3 shows the concentration of the components in the solution and their corresponding adsorbed concentration. For all solution compositions, the preferentially adsorbed species is butanol, with adsorbed concentrations only slightly lower than the saturation concentration. The adsorbed concentrations of acetone and ethanol are in general low but with a higher concentration of acetone over ethanol, as expected from the adsorption isotherms (see Sect. 3.1). This shows that the zeolite is quite selective towards butanol; however more tests should be performed on real fermentation broths to validate the performance in the presence of other potential adsorbates/foulants.

3.2.2 Adsorption of butyric acid and acetic acid mixture

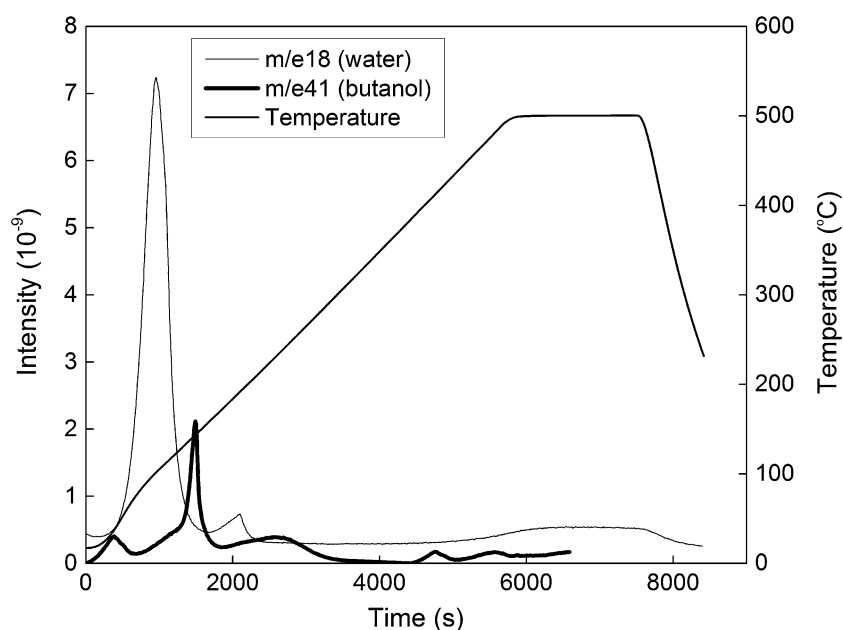
Adsorption experiments with model fermentation solutions of acetic and butyric acid at pH 6 and at concentrations similar to those that may be expected in the fermentation broth were also conducted. Table 3 shows the concentration in solutions and the corresponding adsorbed

concentrations. As expected from the adsorption isotherms (see Sect. 3.1), butyric acid showed a much higher affinity for the high silica zeolite than did acetic acid, in fact, at the conditions studied, no acetic acid was adsorbed.

From these batch adsorption experiments it can be concluded that both butanol and butyric acid adsorb preferentially as compared to the other main components that may be found in the fermentation broth like acetone, butanol, ethanol and acetic acid.

3.2.3 Thermal desorption of butanol

One possible way of desorbing the adsorbed butanol from the zeolite would be to heat the adsorbent. To determine at which temperature butanol desorbs from the zeolite, an experiment was performed using TG-MS. The sample was obtained in the same way as the single component batch adsorption samples and the butanol loading was 0.1 g/g. Figure 4 shows the temperature as a function of time as well as the signal for water (m/e18) and butanol (m/e41) as detected by the MS. Desorption takes place in different steps, first at about 50–55 °C capillary water and butanol, present in the voids between the zeolite crystals desorbs. When the temperature was further increased to about 100 °C adsorbed water started to desorb as shown in Fig. 4 as an intense peak in the water signal. As the temperature was further increased to about 120 °C, the rate of desorption of butanol increased significantly as indicated by the sharp peak in the butanol signal at about 150 °C. As the temperature was further increased, more strongly bounded butanol and water was desorbed. Very similar desorption behavior for high silica MFI zeolite was previously reported by Saravanan et al. (2010) and Milestone and

Fig. 4 Desorption characteristic of the MFI zeolite loaded with butanol and water as determined by TG-MS

Bibby (1983). The generation of the zeolite is a critical step as it influences the overall economy of the process. It would be interesting to compare this data with some other adsorbent currently used in industrial applications e.g. activated carbon or to use different solvents to elute the butanol. This will give a better idea about the economic feasibility of this process.

In summary, the present study shows that adsorption by MFI zeolite can be a feasible way to recover the targeted chemicals (butanol or butyric acid) from ABE fermentation broths. However, more studies should be performed on real fermentation broths and breakthrough experiments simulating the recovery process should be performed. Also, alternative routes for eluting the components from the zeolite should be explored.

4 Conclusions

In this work, a commercial high silica MFI zeolite was assessed as a possible option for recovery of butanol alternatively butyric acid from ABE fermentation broths by adsorption. Adsorption isotherms of butanol, acetone, ethanol, butyric- and acetic acid in MFI were determined and the data were fitted to the Langmuir adsorption isotherm model with good fit. Butanol and butyric acid showed a significantly higher affinity for the zeolite than the other components. Langmuir parameters extracted from the data were in the same range as previously reported data. The adsorption of the acids was found to be strongly pH dependent, with high adsorption below- and little adsorption above the pK_a value of the acids, which opens up for controlled adsorption of desired products. Moreover, adsorption from multicomponent mixtures confirmed the high selectivity of the MFI adsorbent to butanol and butyric acid.

Desorption studies of butanol loaded MFI showed that most of the water desorbed in the temperature interval of 55–120 °C whereas the most intense desorption of butanol took place in the 120–160 °C.

The results obtained so far are encouraging; however more experiments should be performed using real fermentation broths and column breakthrough experiments. Moreover other ways of eluting the products should be explored.

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References

- Bowen, T.C., Vane, L.M.: Ethanol, acetic acid and water adsorption from binary and ternary liquid mixtures on high silica zeolites. *Langmuir* **22**, 3721–3727 (2006)
- Cascone, R.: Biobutanol—a replacement for bioethanol? *Chem. Eng. Prog.* **104**, S4–S9 (2008)
- Durre, P.: New insights and novel developments in clostridial acetone/butanol/isopropanol fermentation. *Appl. Microbiol. Biotechnol.* **49**, 639–648 (1998)
- Ezeji, T.C., Qureshi, N., Blaschek, H.P.: Butanol fermentation research upstream and downstream manipulations. *Chem. Rec.* **4**, 305–314 (2004)
- Ezeji, T.C., Qureshi, N., Blaschek, H.P.: Bioproduction of butanol from biomass: from gases to bioreactors. *Curr. Opin. Biotechnol.* **18**, 220–227 (2007)
- Garcia, V., Pääkkilä, J., Ojamo, H., Murrinen, E., Keiski, R.L.: Challenges in biobutanol production: how to improve the efficiency? *Renew. Sustain. Energy Rev.* **15**, 964–980 (2011)
- Immerseel, F.V., Boyen, F., Gantoist, I., Timbermont, L., Bohez, L., Pasmans, F., Haesebrouck, F., Ducatelle, R.: Supplementation of coated butyric acid in the feed reduces colonization and shedding of *Salmonella* in poultry. *Pollut. Sci.* **84**, 1851–1856 (2005)
- Jin, C., Yao, M., Liu, H., Lee, C.F., Ji, J.: Progress in the production and application of *n*-butanol as a biofuel. *Renew. Sustain. Energy Rev.* **15**, 4080–4106 (2011)
- Maddox, I.S.: Use of silicalite for the adsorption of *n*-butanol from fermentation liquors. *Biotechnol. Lett.* **4**, 759–760 (1982)
- Meagher, M., Qureshi, N., Hutkins, R. (1998) Silicalite membrane and method for selective recovery and concentration of acetone and 1-butanol from model ABE solutions and fermentation broth, US Patent 5755967
- Milestone, N.B., Bibby, D.M.: Concentrations of alcohols by adsorption on silicalite. *J. Chem. Technol. Biotechnol.* **31**, 732–736 (1981)
- Milestone, N.B., Bibby, D.M.: Adsorption of alcohols from aqueous solutions by ZSM-5. *J. Chem. Technol. Biotechnol.* **34A**, 73–79 (1983)
- Oudshoorn, A., van der Wielen, L.A.M., Straathof, A.J.J.: Adsorption equilibria of bio-based butanol solutions using zeolite. *Biochem. Eng. J.* **48**, 99–103 (2009a)
- Oudshoorn, A., van der Wielen, L.A.M., Straathof, A.J.J.: Assessment of option for selective 1-butanol recovery from aqueous solutions. *Ind. Eng. Chem. Res.* **48**, 7325–7336 (2009b)
- Qureshi, N., Hughes, S., Maddox, I.S., Cotta, M.A.: Energy efficient recovery of butanol from model solutions and fermentation broth by adsorption. *Bioprocess Biosyst. Eng.* **27**, 215–222 (2005)
- Saravanan, V., Waijers, D.A., Ziari, M., Noordermeer, M.A.: Recovery of 1-butanol from aqueous solutions using zeolite ZSM-5 with a high Si/Al ratio; suitability of a column process for industrial applications. *Biochem. Eng. J.* **49**, 33–39 (2010)
- Woods, D.R.: The genetic engineering of microbial solvent production. *Trends Biotechnol.* **13**, 259–264 (1995)