Pervaporative separation and intensification of downstream recovery of acetone-butanol-ethanol (ABE)

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ABSTRACT

The feasibility of pervaporative concentration of organic compounds from an ABE mixture to reduce the energy consumption of a downstream recovery unit was investigated. Firstly, an experimental investigation was done, using a polydimethylsiloxane (PDMS) membrane and a model solution of ABE as the feed. Different operating temperatures where investigated, with 40 °C showing the most favourable results. Secondly, the experimental results were utilised as the input for process simulations using Aspen Plus. Two ABE separation schemes were studied, one consisting of only distillation (conventional process) and one with an upstream pervaporation unit followed by an alternative distillation scheme. For the proposed pervaporative scheme, the butanol concentration after pervaporation was high enough so that it could be concentrated further at the beginning of the separation train through a liquid-liquid separation. The results of the simulations indicated that the conventional scheme was the most energy intensive and that the integration with an upstream pervaporation unit decreased energy consumption with 53%. The energy requirement for the distillation scheme was 33.3 MJ kg^{-1} butanol, while that of the pervaporation-distillation scheme was 15.7 MJ kg^{-1} butanol.

1. Introduction

Biofuels and the production of biobutanol have gained increased attention in recent years as an alternative fuel source to conventional fossil fuels produced from coal, oil and natural gas. Fossil fuels have been the main source of energy and fuels for many years. However, due to the growing concern of environmental aspects, such as the emission of greenhouse gases and the global climate change, as well as limited reserves of these resources, alternative fuels are being researched and implemented [1–3]. Biobutanol is considered a favourable alternative fuel due to its high heating value, low volatility and high viscosity (reduces corrosion of fuel engines and pipelines). Butanol is also safer to use, less hydroscopic and can easily be blended with gasoline and other fuels [3–5]. Biobutanol is produced during the fermentation of carbohydrates by *Clostridium* strains such as *Clostridium acetobutylicum*, which yields a mixture of acetone, butanol, ethanol (ABE) and water [4–7]. The ABE fermentation process suffers from certain drawbacks such as high cost of substrates (starch and sugar, such as corn and molasses), low fermentation product concentration and high recovery costs. Due to ABE toxicity towards the micro-organism, the total ABE concentration is below 2 wt.% to prevent the discontinuation of *Clostridia* cellular metabolism, consequently increasing the recovery costs of butanol in the downstream separation unit [2,3,8]. Distillation is the conventional

method for recovery of ABE. It is however an energy intensive process, requiring 18–79.5 MJ kg^{-1} butanol, depending on the pre-treatment step and separation scheme. The lowest number of the reported range is already 50% of the heating value of butanol (36 MJ kg^{-1}) [9–11]. For this reason, alternative separation methods have been investigated to concentrate the butanol feed stream to the downstream distillation unit, prevent butanol toxicity and also to reduce the energy usage. The proposed intensification steps include, gas-stripping, liquid-liquid extraction and membrane separation such as pervaporation and reverse osmosis in combination with distillation [3–5,8,11–15].

Pervaporation is a membrane-based separation method, where the liquid feed contacts one side of the membrane and the permeated product is removed at a lower vapour pressure on the product side. The driving force for the mass transport is a difference in chemical potential across the membrane, which is created by reducing the permeate vapour pressure to below that of the fugacity of the component in the liquid feed [16]. Pervaporation is claimed to be a favourable method of separation due to the fact that it can be integrated with the fermentation process so that the inhibitory products can be removed continuously, thereby enhancing the productivity of the fermentation process [17]. It also has a high separation factor and is harmless towards the micro-organisms [5,18]. Numerous studies have been done on the pervaporative recovery of butanol from both model ABE

Nomenclature		$\frac{PM_i}{l}$	Membrane permeance of component i [g m^{-2} h^{-1} kPa^{-1}]
		p^p	Permeate pressure [kPa]
A	Membrane area [m^2]	R	Universal gas constant [8.314 J mol^{-1} K^{-1}]
A_{ij}, B_{ij}	NRTL binary interaction coefficients of component i an j [-]	t	Time of permeation [h]
		T	Temperature [K or °C]
C_{ij}	NRTL non-randomness factor [-]	W	Permeate mass [g]
$E_{gas\ stripping}$	Energy requirement of gas stripping [MJ kg^{-1} Butanol]	x	Mass fraction in retentate [-]
E_J	Apparent activation energy [kJ mol^{-1}]	y	Mass fraction in permeate [-]
E_p	Permeation activation energy [kJ mol^{-1}]	X	Mole fraction in retentate [-]
ΔH_v	Enthalpy of vaporisation [kJ mol^{-1}]	Y	Mole fraction in permeate [-]
J	Permeation flux [g m^{-2}h^{-1}]	α	Membrane selectivity [-]
J_0	Permeate rate constant [g m^{-2}h^{-1}]	β	Separation factor [-]
l	Membrane thickness [m]	γ	Activity coefficient [-]
$m_{butanol}$	Mass of butanol per unit volume [g L^{-1}]		
M_i	Mole of i per unit volume [mol L^{-1}]		

solutions and fermentation broths. Most of the studies concluded that pervaporation is a favourable method to concentrate the ABE solution and recover butanol [17,19–23].

Pervaporation is affected by different factors such as membrane material, operating temperature, feed flow rate and feed concentration. Operating temperature typically increases the permeation flux, but can have a varying effect on the separation factor of the different components [17,22,24,25]. Studies have also found that the flux and separation factor tend to decrease after a certain time, which is related to the feed concentration of ABE and water. For these studies the retentate was not recycled back to the feed tank or the feed concentration was purposefully varied [14,19]. The fluxes of the organic solvents typically increase with feed concentration because of the increase in partial pressure, while the separation factor tends to decrease [17,22,25,26].

In order to obtain high purity products, distillation is still required, however, by adding pervaporation as a pre-treatment step to concentrate the feed stream, the downstream recovery can be intensified to a point where even the separation sequence can be modified. In this study, an alternative pervaporation-distillation process will be investigated utilising experimental pervaporation results and simulating a pervaporation-distillation scheme in Aspen Plus to obtain commercial grade products (purity > 99.9 wt.%). A new separation scheme is based on a scheme suggested by Bîldea et al. [27], in which the butanol is removed at the beginning of the sequence. For the study by Bîldea et al. [27] the separation scheme was combined with a gas-stripping pre-treatment step, however, for the present study pervaporation will be used to concentrate the feed stream. The aim of this study is to investigate the feasibility of adding a pervaporation unit as a pre-treatment step to concentrate the organic ABE feed before distillation. This will be done by experimentally investigating the pervaporative separation of ABE from a model ABE solution using a PDMS membrane and studying the performance of pervaporation and the influence of operating temperature. The results of the experimental conditions, that give the best butanol recovery and purity, will then be used to simulate a downstream recovery scheme for butanol using Aspen Plus. Both the pervaporation unit and distillation units will be simulated to evaluate the entire separation process. The simulation will be evaluated in terms of energy consumption and butanol recovery and compared to a conventional distillation scheme for ABE, to investigate the extent of process intensification by combining pervaporation with distillation.

2. Materials and methods

2.1. Materials

A model ABE solution was prepared using analytical grade acetone, n-butanol and ethanol. The total solvent concentration was 2 wt.% in demineralised water. The weight ratio in the solvent was 3:6:1 for acetone, butanol and ethanol respectively and corresponds to the typical composition of an ABE fermentation broth [28].

2.2. Pervaporation

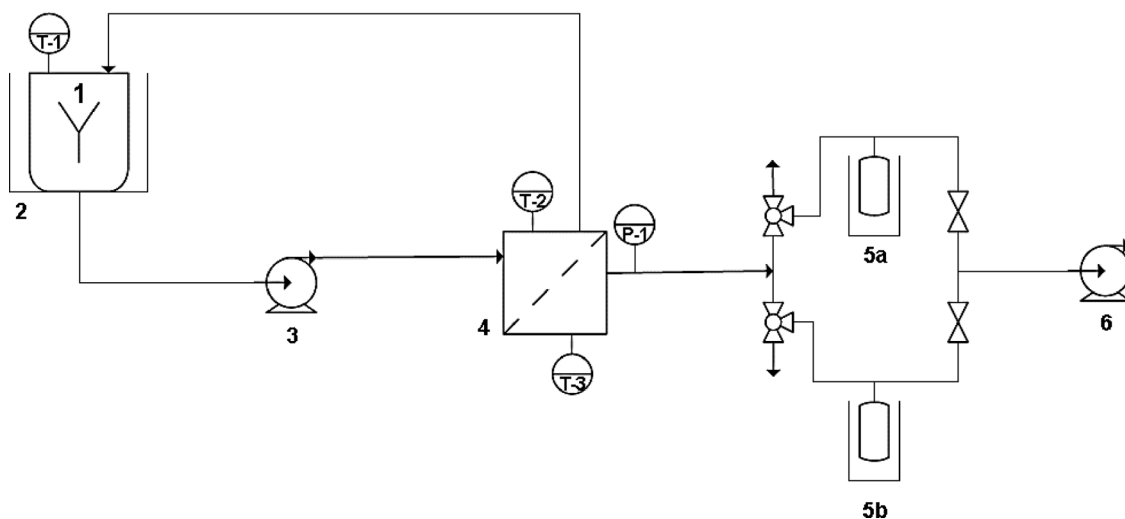Pervaporation experiments were performed using a laboratory scale

Fig. 1. Pervaporation rig (1- Feed tank with mixer; 2 – Water bath; 3 – Circulation pump; 4 – Membrane unit; 5 a&b – Cold traps; 6 – Vacuum pump).

pervaporation rig presented in Fig. 1.

A PDMS on polyimide, membrane (supplied by Pervatech) with an effective area of 44.2 cm^2 was used for the experiments. PDMS membranes are the most commonly used membranes for ABE pervaporation due to their thermal, chemical and mechanical stability. This specific membrane was used in previous studies [10,29] with satisfying results and was therefore selected for this study. The tank was filled with 1 l of ABE solution, which was pumped to the membrane unit. The flow rate of the pump was set to its maximum of 4 L/min (to reduce mass transfer limitations due to the boundary layer effect) which gave an inlet cross-flow velocity of 0.057 m/s. The temperature of the feed tank was controlled with a thermostat (Julabo thermostat). The temperatures investigated for the membrane unit ranged from 20 to 50 °C, while the permeate pressure was set to 0.54 mbar to create a driving force for transport across the membrane. To ensure maximum contact with the membrane surface area, the liquid feed entered at the top side of the membrane unit and flowed radially over the membrane towards the centre where it exited the membrane unit. The liquid retentate was pumped back to the top of the feed tank. The permeate moved through the membrane and exited the unit as a vapour, due to the low pressure on the permeate side created by the vacuum pump. The vapour permeate was condensed in one of the cold traps containing liquid nitrogen. Samples were taken every one to two hours depending on the flux. The mass balance of the acetone, butanol and ethanol closed within 95%. Pervaporation experiments at 30 and 40 °C were repeated two times to determine the reproducibility of the pervaporation rig. Between these tests, the maximum observed difference was 10% in the concentration of ABE.

2.3. Liquid analysis

The composition of the feed/retentate and permeate samples were determined utilising both high performance liquid chromatography (HPLC - Agilent Technologies 1200 HPLC Liquid Chromatography System) and an ultra-visible (UV) spectrophotometer (DR 5000 UV/VIS Spectrophotometer by Hach-Lange). UV analysis (wavelength: 264 nm) was done to determine the acetone concentration. From the UV determined acetone concentration, the ethanol concentration could be indirectly calculated, as the HPLC measures the collective acetone and ethanol concentration. The butanol content was directly measured using HPLC. The permeate samples were diluted with demineralised water to ensure a homogenous sample for HPLC analysis. For the UV analysis the samples were diluted with demineralised water to ensure that the concentrations fell within the linear range of the Lambert-Beer law. All analyses were repeated twice to measure the reproducibility,

with the experimental errors being < 3% (95% confidence level interval).

2.4. Pervaporation performance equations

The performance of the pervaporation unit was evaluated by estimating both the flux, J (g m^{-2} h^{-1}) and separation factor (β) [16,30]:

$$J_{\Delta t} = \frac{W_{\Delta t}}{A \cdot \Delta t} \tag{1}$$

$$\beta_i = \frac{y_i/(1-y_i)}{x_i/(1-x_i)} \tag{2}$$

Where W (g) is the mass of the permeate taken over the time period Δt, A (m^2) is the membrane area (0.00044 m^2), Δt (h) is the time over which the sample was taken and y_i and x_i (-) are the mass fractions of components i in the permeate and retentate respectively. The partial flux (J_i) of the individual components was also determined as a function of the total flux [19]:

$$J_i = y_i \cdot J \tag{3}$$

The membrane permeance of the individual components was determined using the pervaporation transportation equation, which is based on the solution-diffusion model [20]:

$$\left[\frac{PM_i}{l}\right] = \frac{J_i}{(X_i \gamma_i p_i^{sat} - Y_i p^p)} \tag{4}$$

Where $\frac{PM_i}{l}$ (g m^{-2} h^{-1} kPa^{-1}) is the membrane permeance of component i. Y_i and X_i (-) are the molar fractions in the permeate and feed respectively. p_i^{sat} (kPa) is the saturated vapour pressure of the pure compound i at 30 °C (operating temperature) and was determined using the Antoine equation. p^p (kPa) is the permeate pressure. The activity coefficients (γ_i) was calculated using Aspen Plus V8.8, using the Non-Random Two Liquid (NRTL) model. Lastly, the membrane selectivity was determined from the permeances [30]:

$$\alpha_{ij} = \frac{PM_i}{PM_j} \tag{5}$$

3. Experimental results

Firstly, the performance of pervaporation is discussed in terms of the permeate concentration, partial flux and separation factor of the different components at 30 °C. The performance of the membrane itself is also discussed in terms of the permeance and selectivity. Next, the
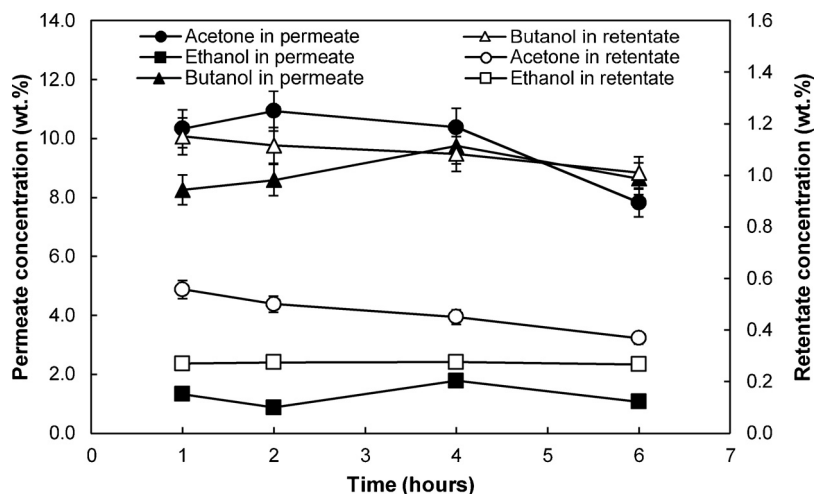
Fig. 2. Permeate and retentate composition as a function of operating time at 30 °C (For the ethanol results error bars were also added, but are not visible due to the low concentrations; line serves as guide to the eye).

effect of operating temperature on the pervaporation performance is examined in terms of the apparent activation energy along with the previously mentioned parameters. From the results, conditions were selected for the simulation of the downstream recovery process.

3.1. Pervaporation performance

The influence of feed concentration is examined by comparing the permeate composition to that of the retentate as a function of time, as shown in Fig. 2.

Firstly, when comparing the acetone permeate concentration with the feed concentration it is seen that after two hours of operation both the feed and permeate concentration decreases, relating positively to each other. For butanol, the permeate concentration slightly increases up to four hours after which it reduces, while the feed concentration gradually decreases with time. The initial increase in the butanol permeate concentration could be due to the coupling effect, where the acetone molecules in the feed hinder the movement of butanol through the membrane. As the acetone feed concentration decreases, the competition between the molecules decreases and butanol is able to move more freely through the membrane [20,31]. When comparing the acetone permeate concentration to that of butanol, it is seen that the initial concentration is higher but decreases with time to below that of butanol. This is due to the reduction in feed concentration of acetone and the increase in butanol permeate amount (concentration). With regards to the ethanol concentration, it is seen that both the feed and permeate concentration remain relatively constant because of the low permeability of ethanol.

The pervaporation performance (flux and separation factor) as a function of the operating time is illustrated in Fig. 3 and 4.

From the partial flux results, it is firstly seen that the productivity of acetone decreases with time, while that of butanol and ethanol seem to remain fairly constant. It is furthermore observed that the fluxes of acetone and butanol are larger in comparison to that of ethanol, indicating a better separation factor towards acetone and butanol by the membrane. Cai et al. [14] and Ren & Jiang [31] explained that the poor separation of ethanol is due to the formation of ethanol-water clusters, which increases the kinetic diameter of the ethanol molecules, thereby impeding the movement through the membrane. Additionally, the membrane is hydrophobic in nature, which contributes to the low diffusivity of the ethanol-water clusters. From the separation factor results, it is seen that acetone has the highest separation factor, followed by butanol and then ethanol. For acetone and butanol, the separation factor slightly increases up to four hours of operation after which it starts to reduce, while the separation factor of ethanol appears to remain constant.

The permeance of acetone, butanol and ethanol is shown in Fig. 5. From Fig. 5 it can be seen that the membrane permeance remains

constant for the given operating time. The fluctuations in the permeance of ethanol is due to the difference between the feed and permeate concentrations being small which translates into large errors in the permeance. The average permeance (over six hours of operation) was also estimated with butanol having the highest average permeance of 440 g m^{-2} h^{-1} kPa^{-1}, followed by acetone, 240 g m^{-2} h^{-1} kPa^{-1} and lastly ethanol, 200 g m^{-2} h^{-1} kPa^{-1}. The estimated permeance for water was 150 g m^{-2} h^{-1} kPa^{-1}.

The permeance of acetone, butanol and ethanol was also determined for 40 °C, with the trend of butanol and acetone remaining similar to that of Fig. 5, while more fluctuations were observed for ethanol. The average permeance was 420 g m^{-2} h^{-1} kPa^{-1} for butanol, 210 g m^{-2} h^{-1} kPa^{-1} for acetone, 250 g m^{-2} h^{-1} kPa^{-1} for ethanol and 120 g m^{-2} h^{-1} kPa^{-1} for water. From the results, it is seen that the permeance for acetone decreases at 40 °C, making ethanol more permeable than acetone, but that the permeance of butanol still remains the highest.

Lastly, the membrane selectivity of acetone, butanol and ethanol was determined with the average values, for 30 °C over four hours, being 1.6, 2.9 and 1.3 for acetone, butanol and ethanol respectively, relative to the water permeance. For 40 °C, the values were also in a similar range.

3.2. Influence of operating temperature

The influence of operating temperature on pervaporation performance was investigated by determining the average flux, separation factor and permeate concentrations over four hours of operation. As shown in Fig. 6, the flux increases exponentially with operating temperature, with the increase of ethanol flux being significantly less in comparison to that of the remaining components.

The increase in flux corresponds to the results reported in numerous studies such as Fouad & Feng [24], Huang & Meagher [32], Liu et al. [17] and Zhou et al. [22]. The reason for the higher flux is the rise in the partial permeance and thereby the driving force of pervaporation. Zhou et al. [22] also stated that an increase in temperature, decreases membrane resistance because of membrane swelling, which in turn facilitates the transport of the components. The separation factor results are presented in Fig. 7 and it is seen that the separation factor of acetone decreases with operating temperature, from 24.8 to 16.5.

For butanol, the separation factor seems to increase up to a temperature of 40 °C after which it remains constant, while the separation factor of ethanol appears to remain constant with temperature. Zhou et al. [22] observed similar trends in the separation factor of the components and stated that the decrease of acetone separation factor was due to acetone having a lower activation energy in comparison to water, which is also seen in the results of this study (see Table 1). By having a higher activation energy, water is more sensitive to a change
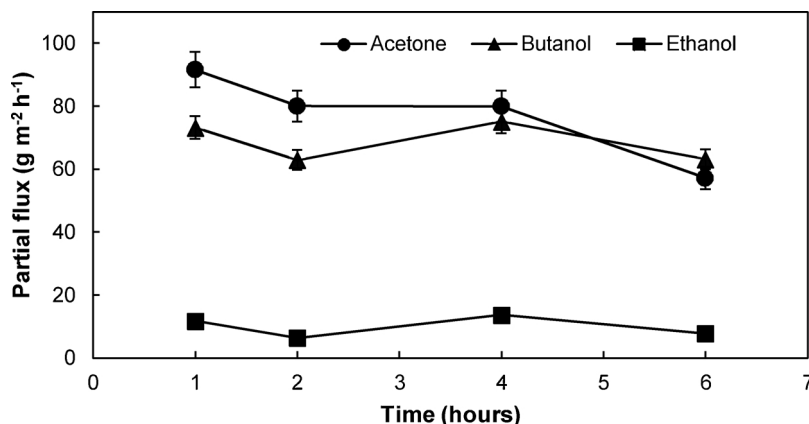

Fig. 3. Permeate flux of acetone, butanol and ethanol as a function of operating time at 30 °C (line serves as guide to the eye).
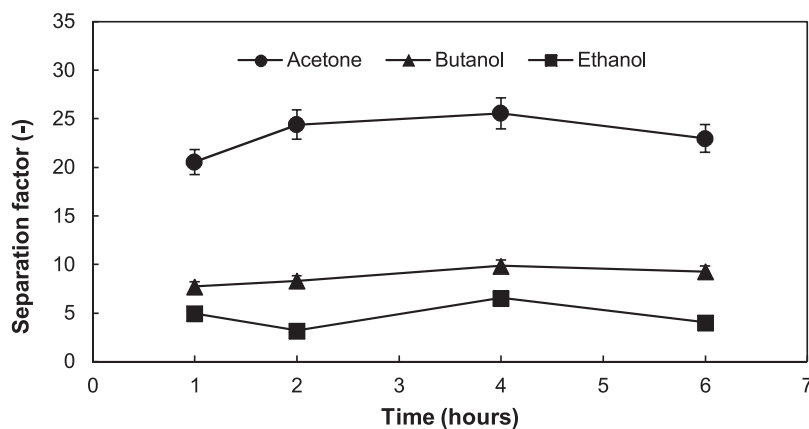
Fig. 4. Acetone, butanol and ethanol separation factor as a function of operating time at 30 °C (line serves as guide to the eye).

in temperature and therefore an increase in temperature would increase the water flux more readily than the acetone flux. This in turn will lead to a decrease in acetone separation factor with temperature. Conversely butanol has a higher activation energy in comparison to water and therefore the flux of butanol will increase more profoundly leading to an increase in butanol separation factor with operating temperature, which is evident from the results in Fig. 7. The apparent activation energy was estimated using the Arrhenius equation, given in Eq.(6) [16,17]:

$$J_i = J_o \, e^{\left(\frac{-E_J}{RT}\right)} \qquad (6)$$

Where J_i (g m^{-2} h^{-1}) is the permeate partial flux of species i, J_o is the permeate rate constant, R (8.314 J mol^{-1} K^{-1}) is the gas constant, T (K) is the operating temperature and E_J (kJ mol^{-1}) is the apparent activation energy. The results in Fig. 8, show that the flux displays an Arrhenius type dependence with temperature.

The estimated apparent and permeation activation energies are given in Table 1.

From the results, it is seen that all the apparent activation energies are positive, indicating that the flux will increase with a rise in operating temperature, corresponding with the results in Fig. 6. The values are also similar to that reported by previous studies [22,24,26]. Butanol has the highest activation energy illustrating, that it is the most sensitive to a change in temperature. This is also shown by the increase in butanol separation factor with operating temperature (see Fig. 7). A higher separation factor of butanol can therefore be achieved by increasing the operating temperature.

The above estimated activation energy, E_J, includes both the effect of temperature on the membrane as well as the driving force for pervaporation. The influence of temperature on the membrane

permeability can be separately evaluated by estimating the permeation activation energy, E_p. Feng & Huang [16] stated that the following equation can be used to estimate the permeation activation energy:

$$E_p = E_J - \Delta H_V \qquad (7)$$

Where ΔH_V (kJ mol^{-1}) is the enthalpy of vaporisation. These values along with the estimated E_P values are given in Table 1. From the results it can be seen that values for all the components are negative, which indicates that the membrane permeability coefficient (permeance) decreases even though the permeation flux increases with temperature [16,22,24].

In summary, when comparing the results of Section 3.1 it is seen that the pervaporation and membrane performance remains fairly stable for the duration of the experiments. For the purpose of the Aspen Plus simulations the results over four hours of separation was chosen as input.

In Table 2 the average butanol permeate concentration, flux and separation factor is presented for the different operating temperatures, as well as the ABE concentration of the feed over four hours.

It is firstly observed, that the permeate concentration of butanol is the highest at 40 °C. Furthermore, it is seen that the separation factor of butanol increases up to 40 °C after which it remains relatively constant. 15% of the organics are removed from the feed/retentate. Moreover, the typical temperature of the fermentation broth is 37 °C [14,21,23] and therefore no additional heating or cooling will be required if the pervaporation unit is integrated with an ABE fermenter. For these reasons, 40 °C was selected as the operating temperature for pervaporation and the corresponding cumulative permeate mass, of each component over four hours, will be used to calculate the split fractions for the simulations of the downstream butanol recovery.
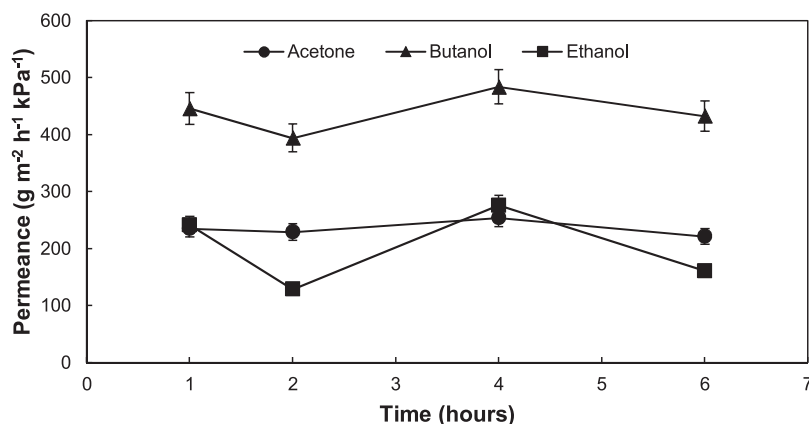

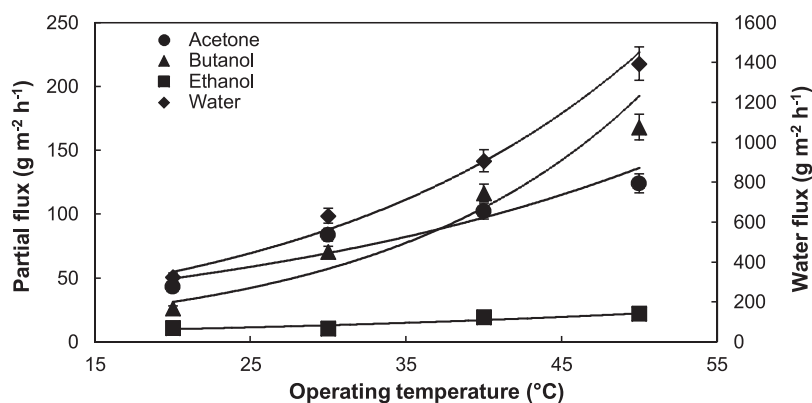**Fig. 5.** Membrane permeance at 30 °C (line serves as guide to the eye).

Fig. 6. Permeate flux of acetone, butanol, ethanol and water as a function of operating temperature (line is an exponential fit).

4. Simulation recovery process

Even though pervaporation is an effective manner of concentrating the ABE feed and recovering butanol, further distillation is still required to achieve commercial grade butanol (purity > 99.9 wt.%), as the ABE solution, after pervaporation, still consists mostly of water (77.6 wt.%; simulated results). Different downstream distillation sequences were simulated in Aspen Plus V 8.8, in order to evaluate the energy consumption and productivity of the pervaporation and distillation units and compare them with a conventional distillation scheme.

4.1. Simulation

The NRTL activity coefficient model was selected for the simulations. This model is able to accurately predict the vapour-liquid equilibrium (VLE) of all components; however, for the butanol-water liquid-liquid equilibrium (LLE) the estimated parameters under predicted the butanol composition in the organic phase. Experimental LLE data from Prochazka et al. [33] (obtained from the National Institute of Standards and Technology (NIST) database), was regressed in Aspen Plus and the estimated parameters were used for the LLE calculations. In Fig. 9, the experimental and model based VLE and LLE results for the butanol-water system are compared.

The interaction coefficients for butanol-water for both the LLE and VLE are given in Table 3.

The remaining interaction coefficients were taken from the Aspen Plus database. The pervaporation unit was simulated using a separator block and a cooler. The split fractions were calculated from the experimental permeate mass results obtained over four hours of

Table 1
Estimated activation energies.

Component	Apparent activation energy - E_J (kJ mol^{-1})	Permeation activation energy - E_P (kJ mol^{-1})	Enthalpy of vaporisation (kJ mol^{-1})[a]
Acetone	26.7	−3.4	30.1
Butanol	48.0	−3.2	51.2
Ethanol	20.9	−20.5	41.4
Water	37.3	−5.5	42.8

[a]Enthalpy of vaporisation at 40 °C obtained from NIST database.

pervaporation at 40 °C, as presented in Table 4.

For the condensation of the vapour permeate stream, a cooler block was used. The pressure was set to 0.54 mbar and the vapour fraction to zero from which the outlet temperature was calculated to be -33 °C. The distillation columns were simulated using RADFRAC columns, which were optimised using design specifications and sensitivity analyses.

4.2. Integration with fermentation

The proposed integration of the downstream recovery process with the fermentation unit is shown for both the conventional distillation and the pervaporation-distillation scheme, in Fig. 10.

The process starts with water, nutrients and carbohydrates being fed to the fermentation unit/units. By comparing Fig. 10 a) & b) it can be seen that for the conventional scheme the cells first need to be removed in an ultrafiltration unit before the ABE feed is sent to the distillation column. The excess water is removed in the first column along with
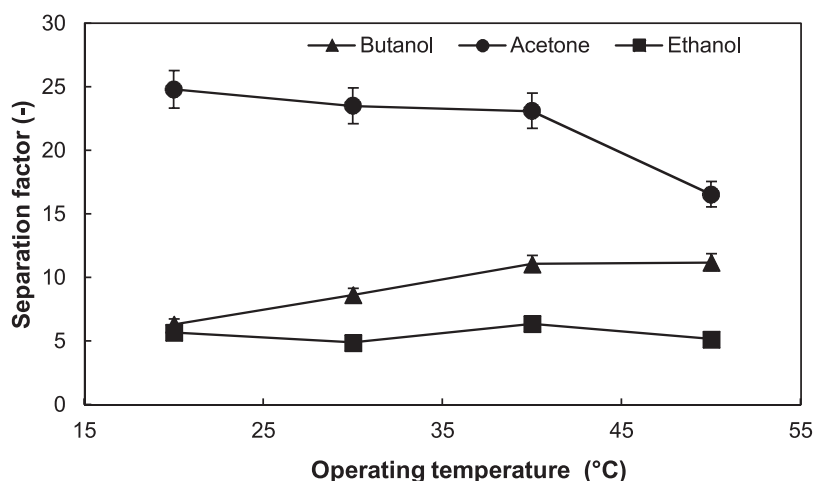

Fig. 7. Acetone, butanol and ethanol separation factor as a function of operating temperature (line serves as guide to the eye).
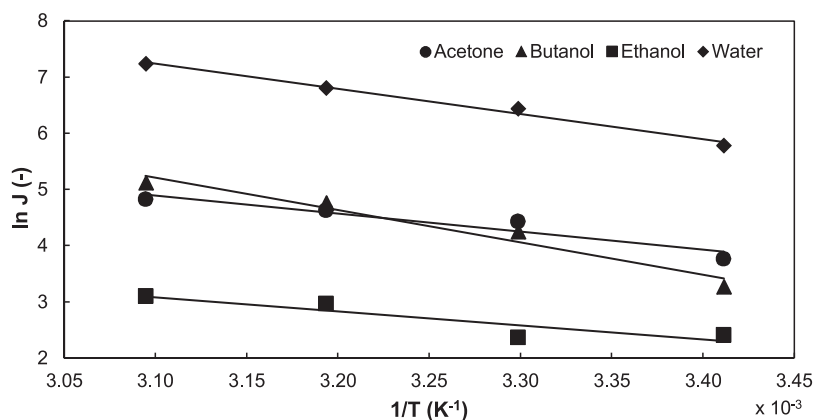
Fig. 8. Arrhenius plot for activation energy calculation (line is a linear fit).

Table 2
Summary of average butanol results for the four different temperatures over four hours.

	20 °C	30 °C	40 °C	50 °C
Butanol permeate concentration (wt.%)	6.7	8.9	10.2	9.8
Butanol flux (g m^{-2} h^{-1})	26.7	71.6	116.6	168.1
Butanol separation factor (-)	6.3	8.6	11.1	11.2
Solvent feed/retentate concentration (wt.%)	2 →1.9	2→1.9	2→1.7	2→1.6

Table 3
NRTL interaction coefficients for butanol-water.

Interaction parameter [a]	LLE (Fitted)	VLE (Aspen Plus)
A_{BuOH,H_2O}	−3.34	−2.04
$A_{H_2O,BuOH}$	6.10	13.11
B_{BuOH,H_2O}	968.43	763.87
$B_{H_2O,BuOH}$	−588.48	−3338.95
C_{BuOH,H_2O}[b]	0.30	0.30

[a]Aspen defined NRTL binary interaction parameters.
[b]Non-randomness factor (α).

Table 4
Estimated split factions for pervaporation simulation.

Component	Split fraction[a]
Acetone	0.360
Butanol	0.190
Ethanol	0.122
Water	0.017

[a]Split fraction = (total permeate mass over 4 h/ initial feed mass) of component *i*.

some unconverted acetic acid, butyric acid and dissolved carbohydrates. This stream then needs to be further processed to purify the water. For the pervaporation scheme, both the cells and water as well as additional minerals and remaining carbohydrates stay in the retentate, which is directly recycled to the fermentation unit. Fouling could occur, however, the membrane can be cleaned with water or an ultrafiltration unit (pre-treatment step) could be added [5,23]. Depending on the type of feed stock used a purge stream from the recycle might be required to remove the excess unreacted carbohydrates and salts. Sugars such as glucose have been shown to be fully utilised for fermentation; however, sugars such as xylose will not react completely leading to a build-up of unreacted carbohydrates [34]. The purge stream can either be sent to a third fermenter as proposed by Van Hecke et al. [29,34] for further production of solvents or it can be processed at a water treatment facility. In this case a feed of glucose with full conversion is assumed and therefore a small (negligible) purge is required.

For pervaporation as a pre-treatment step, a continuous fermentation process is proposed. In this manner the feed concentration to the pervaporation unit and consequently the distillation is kept more constant as oppose to batch fermentation, where the concentration of ABE

in the feed to the recovery train will decrease in time, leading to a higher energy requirement. It will also lead to a decrease in the butanol concentration such that liquid-liquid phase separation of the permeate will no longer be possible.
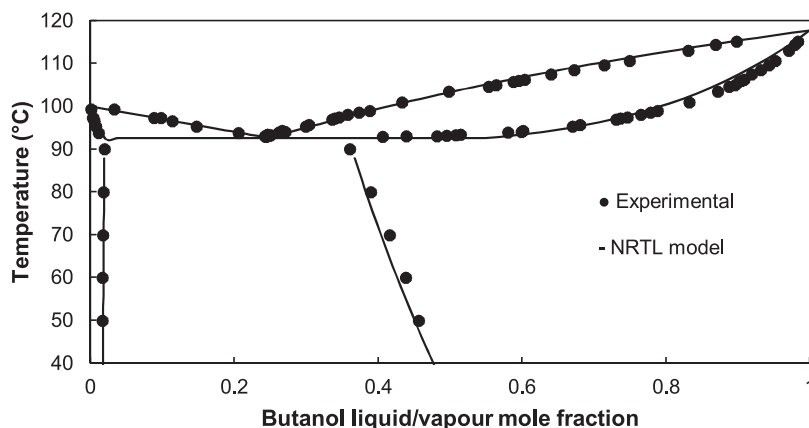

Fig. 9. Phase diagram for butanol-water system (experimental data taken from [33]).
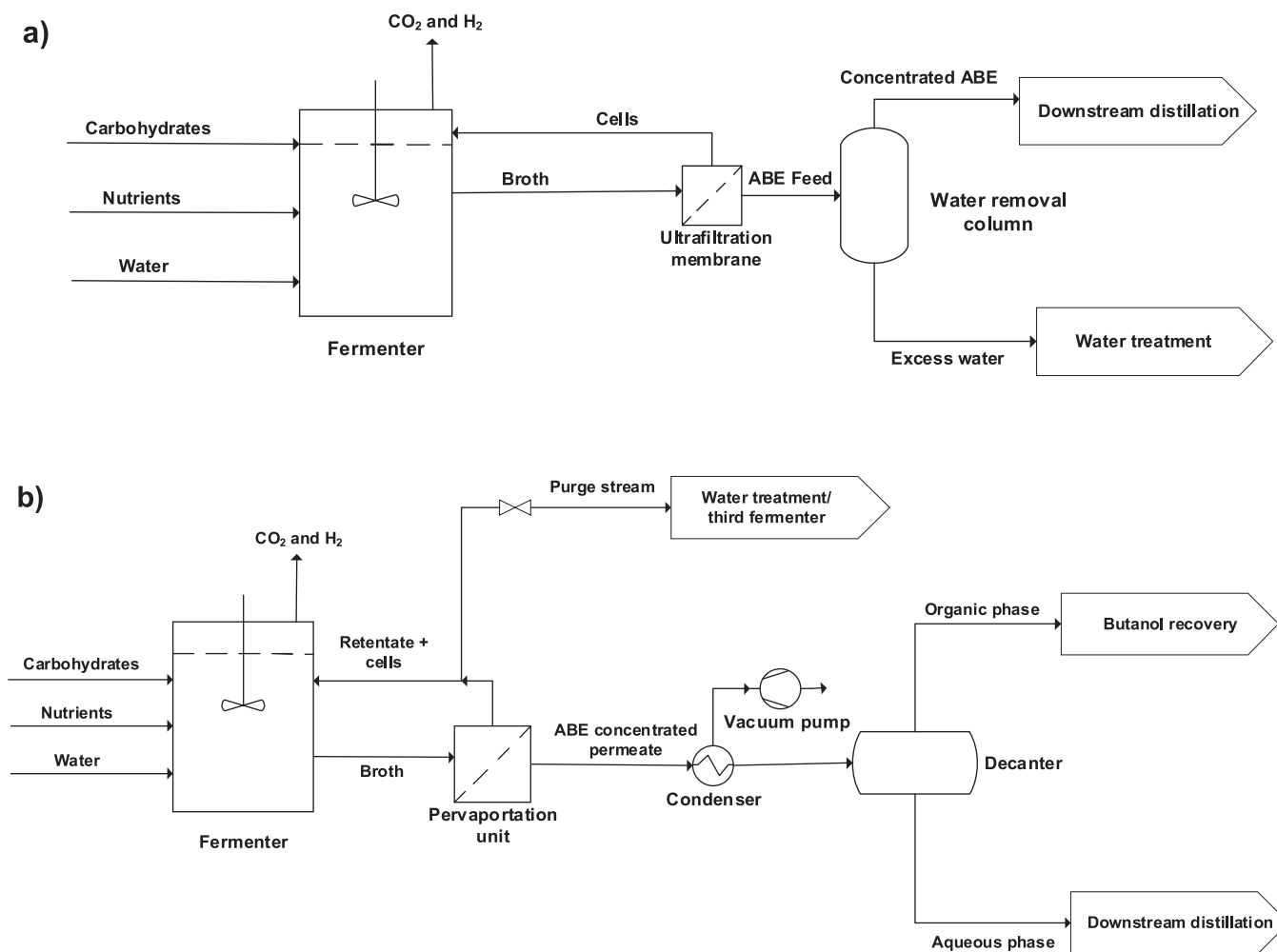
Fig. 10. Integration of downstream recovery with fermentation unit a) conventional distillation scheme, b) pervaporation-distillation scheme.

4.3. Downstream distillation

For both simulations, the feed entered at 40 °C and 1 bar, while the feed flow rate varied to reflect a plant capacity of 40 000 t per annum butanol, assuming the plant is in operation 8000 h per year. The process flow diagrams of the two simulations are given in Figs. 11 and 12.

Firstly, for the conventional distillation scheme (Fig. 11), the feed composition consisted of 0.6, 1.2, 0.2 and 98 wt.% acetone, butanol, ethanol and water respectively, similar to the composition of a typical ABE fermentation broth. The excess water was first removed in W−COL1 to concentrate the stream, with the bottoms being sent for further processing to purify the water. The recovery of the column was set to 98% water, which is similar to the water recovery in the retentate of the pervaporation unit.

Next the acetone (A−COL) was removed followed by a second water removal column (W−COL2). The distillate of W−COL2 is a
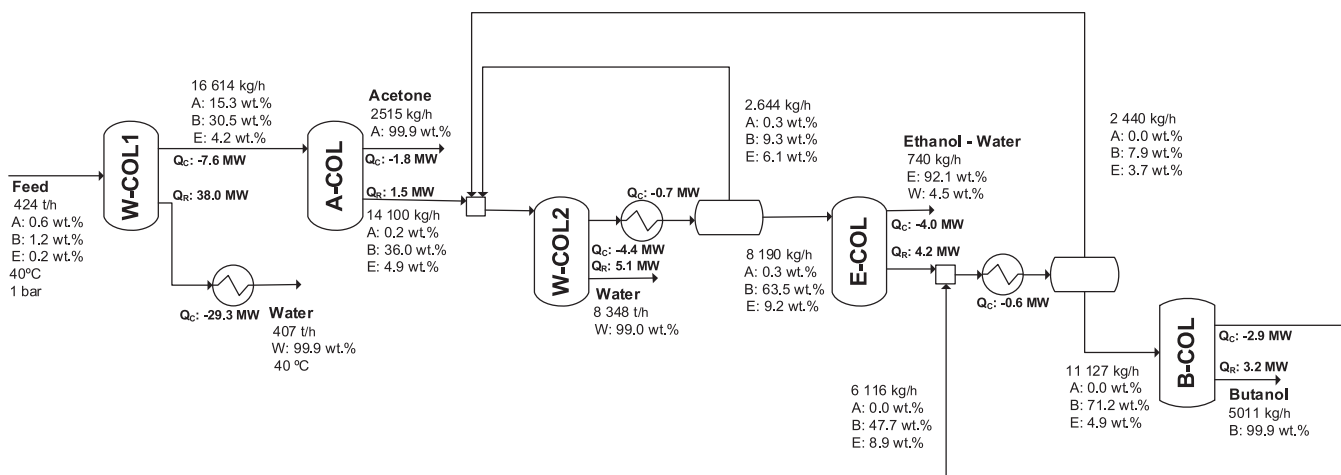

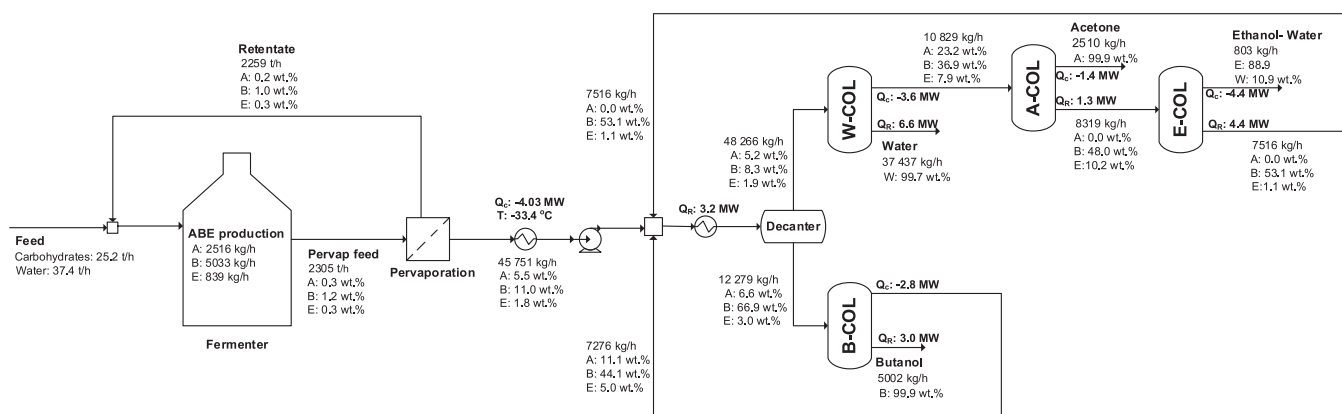**Fig. 11.** Process flow diagram of conventional distillation simulation.

Fig. 12. Process flow diagram of pervaporation - distillation simulation.

heterogeneous azeotrope of butanol/water, which after additional cooling, was separated in a decanter. The aqueous stream is recycled to W−COL2, while the organic rich stream is sent to the ethanol removal column (E−COL), where the ethanol/water azeotrope is recovered at the top. The bottom stream of the column was once again separated in a decanter, with the organic rich stream being sent to the butanol recovery unit (B−COL). E−COL is placed between the water recovery and butanol recovery to prevent the build-up of ethanol in the recycle stream. In this simulation 5 t h^{-1} butanol was produced with a purity of 99.9 wt.%. The overall recovery of butanol was 98.5% (relative to the feed stream) and 98.6% (relative to the distillate of W−COL1).

For the pervaporation-distillation scheme (Fig. 12), the fermenter is simulated by using a mix tank. The recycle stream of the retentate is first mixed with a carbohydrate (25.2 t/h) and water (37.4 t/h) feed, before entering the fermenter. The resulting carbohydrate concentration to the fermenter is 11.2 g kg^{-1} H_2O. The carbohydrates feed was calculated assuming a yield of 0.33 g carbohydrates/g solvents inside the fermenter. Inside the fermenter the micro-organisms produce ABE in the weight ratio of 3:6:1, which is the typical yield for the ABE broth. During fermentation non-condensable gases H_2 and CO_2 are also produced (not simulated). In the case of CO_2, a certain amount of the produced gas will dissolve in water, with the remaining CO_2 and H_2 removed from the top of the fermenter (see Fig. 10). The feed stream to the pervaporation unit consists of 0.3, 1.2 and 0.3 wt.% acetone, butanol and ethanol (total solvent concentration of 1.8 wt.%) with the remaining mass being water. The retentate was directly recycled to the fermenter and consisted of 98.5 wt.% water and 1.5 wt.% ABE solvent. Since the simulation contains ABE and water (based on the results of the model solution experiments), and assumes full carbohydrate conversion, the purge stream is not simulated in this case. The composition of the permeate stream is 5.5 wt.% acetone, 11.0 wt.% butanol, 1.8 wt.% ethanol and 81.7 wt.% water. The stream is thus concentrated enough to facilitate liquid-liquid phase separation between a butanol rich and a water rich phase, with the organic rich stream being sent to B−COL and the aqueous stream to W−COL. In this simulation 5 t h^{-1} of butanol with a purity of 99.9 wt.% was produced. The recovery relative to the feed stream of the pervaporation unit is 18.8% and 99.4% relative to the permeate stream. It can therefore be seen that the choice of membrane should be improved as the butanol recovery of the pervaporation unit is only 18.8%. A membrane with a higher productivity and separation factor, such as a PDMS/ceramic composite or a PDMS zeolite filled membrane [21,23,26], could be considered.

4.4. Energy consumption

For the energy consumption comparison two cases will be examined and compared. Firstly, the idealized case where the presence of non-condensable gases (CO_2 and H_2) in the permeate stream is not considered. This is the case for most pervaporation studies done till thus far. Secondly, a more realistic case will be considered in which the additional energy requirement due to the presence of non-condensable gases in the permeate stream is considered as well as the energy requirement for the downstream processing of the water streams.

4.4.1. Idealized case

Heat integration, using the pinch analysis in Aspen Energy Analyzer V8.8, was done in order to lower the energy consumption of each simulation, assuming a minimum temperature approach of 10 °C for heat exchange. The energy consumption, after heat integration, of the conventional distillation was 33.3 MJ kg^{-1} butanol, while that of the pervaporation-distillation scheme was 9.7 MJ kg^{-1} butanol, which corresponds to only 27% of the butanol heating value (36 MJ kg^{-1}). The energy consumption calculation was based on the energy requirement of the reboilers and duty for condensation in the pervaporation unit (after heat integration) as seen in Table 5.

It is seen that the addition of a pervaporation unit is able to decrease the energy consumption with ± 71%. The most energy intensive unit for both simulations, is the reboiler of the water recovery column. In Table 6, the energy consumption of conventional distillation and distillation coupled with pervaporation and/or gas-stripping, is presented.

From the comparison of Tables 5 and 6, it is firstly seen that the reported energy requirement for conventional distillation is lower in comparison to that of the present study. These differences are mainly attributed to the presence of the second water recovery column (W−COL2) and also the higher recovery of the ethanol/water azeotrope in E−COL. For the pervaporation-distillation schemes it is seen that the energy requirement varies between 4.2–14.6 MJ kg^{-1} butanol, with the lowest energy requirement being due to a high separation efficiency of the pervaporation unit (separation factor of 100 for butanol). The energy requirement for gas-stripping is higher in comparison to that of pervaporation-distillation, even when a pervaporation unit is also added to further concentrate the feed. When comparing the results of the energy consumption of our proposed pervaporation-distillation scheme to that reported in Table 6, it is seen that in general the

Table 5
Heating and refrigeration demands of downstream recovery schemes.

	Distillation	Pervaporation-distillation[b]
Total energy demand of reboilers (MJ kg^{-1})	33.3	8.5
Total refrigeration requirement, T = -33 °C (MJ kg^{-1})[a]	–	1.2

[a] Electric energy requirement for cooling was multiplied by 2 to reflect thermal energy requirement.
[b] Heat of evaporation is also included but is minimal = 0.019 M kg-1 butanol.

Table 6

Energy consumption of different ABE recovery schemes published in literature.

Separation scheme	Energy consumption (MJ kg^{-1} butanol)	Reference
Conventional distillation	18.4; 21.4	[9,10]
Pervaporation-distillation	4.2 – 14.6; 13.8	[10,35]
Gas-stripping-distillation	5.1; 26.3	[14,27]
Gas-stripping-pervaporation-distillation	23.3	[14]
Two stage pervaporation-distillation	13.2	[36]

energy requirement for the scheme presented in Fig. 12 is lower; with the exception of the gas-stripping-distillation scheme of Bîldea et al. [27] at 5.1 MJ kg^{-1} butanol and the pervaporation schemes of Van Hecke et al. [10] at 4.2 MJ kg^{-1} butanol who estimated the energy requirement based on high separation factors (25–100).

All the above distillation schemes, with the exception of Bîldea et al. [27], follow a conventional separation train, as given in Fig. 11 (Section 4.3). Upon comparing the energy consumption of our pervaporation separation scheme to that of Bîldea et al. [27], it is seen that their energy requirement is lower. The total estimated energy requirement was 5.1 MJ kg^{-1} butanol. This is due to Bîldea et al. [27] having a more concentrated feed stream as a result of the upstream gas-stripping unit. The energy requirement for the gas-stripping was not considered for the calculations. If the required energy of the integrated pervaporation unit (after heat integration 1.2 MJ kg^{-1}), for this study, is subtracted, the energy consumption reduces to 8.5 MJ kg^{-1} butanol, which is still higher in comparison to Bîldea et al. [27]. However, if the feed concentrations and feed rate of their study is utilised as the feed conditions of the current simulation (excluding pervaporation), the total energy consumption reduces to 4.6 MJ kg^{-1} butanol. It can thus be seen that increasing the feed concentration will reduce the energy costs and therefore a membrane with a higher separation factor, specifically towards butanol, needs to be utilised. Preliminary energy calculations were done to estimate the energy requirement of gas-stripping for the study of Bîldea et al. [27], [14]:

$$E_{gas\ stripping} = \sum \frac{\Delta H_v \times M_i}{m_{Butanol}} \tag{8}$$

With $E_{gas\ stripping}$ (MJ kg^{-1} butanol) being the gas stripping energy requirement, M_i (mol L^{-1}) mole per unit volume, and $m_{Butanol}$ (g L^{-1}) the mass of butanol produced per unit volume. The results revealed that 10.5 MJ kg^{-1} butanol (assuming the stream is at 40 °C) is required to concentrate the feed stream, therefore making the total energy requirement of the process 15.6 MJ kg^{-1} butanol.

Lastly, simulations were done to determine what the butanol separation factor of the membrane should be, so that the total energy consumption is below 4 MJ kg^{-1} butanol for the idealized case. For the simulations, the separation factor of acetone and ethanol were set to reflect a permeate concentration similar to the feed concentration of Bîldea et al. [27] and kept constant while the separation factor of butanol and water was varied. The results showed that separation factor of butanol should be ± 36 (instead of the currently used value of ± 10), which will result in a total energy consumption of 3.7 MJ kg^{-1} butanol (including refrigeration of pervaporation), after heat integration. From previous studies, it is seen that PDMS/silicone based composite membranes filled with silicalite, such as those used by Fouad & Feng [24], Huang & Meagher [32], Qureshi et al. [37] and Zhou et al. [22], are able to give the desired butanol separation factor.

4.4.2. Realistic case

For the more realistic case two aspects that are typically neglected during the energy requirement studies, are addressed. These two aspects are the presence of non-condensable gases in the permeate stream

and the energy requirement for the treatment of the water stream, both of which will increase the energy consumption of the process.

4.4.2.1. Non-condensable gases. As mentioned for the realistic case the presence of non-condensable gases, namely H_2 and CO_2, is also considered for the energy costs. According to Van Hecke & De Wever [34] 2.6 mol of CO_2 and 1.59 mol of H_2 is generated per mole of solvent (ABE) during fermentation. For the simulation described in Fig. 12 the total amount of produced solvents (micro-organism ABE composition) in the fermenter is 129 kmol h^{-1}. Therefore, 14 810 kg h^{-1} of CO_2 and 416 kg h^{-1} of H_2 is produced for the given process.

The gas that is fed to the pervaporation unit is dissolved in the solution to the unit. The solubility of CO_2 and H_2 in water at 40 °C was estimated using Henry's law assuming a total pressure of two bar inside the reactor (one bar headspace and one bar hydrostatic pressure). The estimated solubilities were 1.24 g CO_2 kg^{-1} H_2O and 0.001 g H_2 kg^{-1} H_2O. Since the solubility of H_2 is very low compared to that of CO_2, only CO_2 was considered. The total amount of CO_2 dissolved in the feed stream to the pervaporation unit is 2807 kg h^{-1}. Calculations for the energy requirement were done for 100, 50 and 10% of dissolved CO_2 (in the pervap water feed stream (2264 t h^{-1})), passing through the membrane.

The electric energy required by the vacuum pump was determined by simulating the pervaporation permeate stream (see Fig. 12) along with the estimated CO_2 in the stream. The stream is first separated into a liquid and gas stream (flash) with the gas stream sent to a compressor to compress the gas from 0.00054 to 1 bar. An isentropic efficiency of 80% was assumed for the compressor. The estimated electrical power is then multiplied with a factor two for thermal energy and divided by the total amount of butanol produced to give the energy requirement in MJ kg^{-1} butanol. The results are summarised in Table 7.

From the calculations it can be seen if all the dissolved CO_2 were to move through the membrane the total energy requirement of the pervaporation-distillation scheme would be 15.7 MJ kg^{-1} butanol, which is still less than half (44%) of the energy requirement of the base case. For 50% of CO_2 the total energy requirement increases to 13.4 MJ kg^{-1} butanol, while for 10% of CO_2 the total energy consumption becomes 11.1 MJ kg^{-1} butanol, which is 31% of the butanol energy content.

Typically laboratory scale pervaporation studies are performed at permeate pressures of 0.5–4 mbar [14,19–21,36], however industrially, permeate pressure of 10–50 mbar are applied [40]. The applied permeate pressure will affect the energy requirement of the vacuum pump. Van Hecke & De Wever [34] showed that for permeate pressures below 15 mbar the power consumptions exponentially rises and therefore operating at higher permeate pressures could be energetically favourable for the process. Even though the energy consumption of the pump decreases, the driving force for pervaporation will also decrease and increase the required amount of membrane surface area. Future studies are therefore required to determine an optimum permeate pressure to reduce energy consumption while still maintaining a suitable production of concentrated solvents.

Table 7

Vacuum pump energy requirement for varying CO_2 permeate flows.

	100% CO_2[a]	50% CO_2[a]	10% CO_2[a]
Amount of CO_2 (kg h^{-1})	2807	1403	281
Electrical energy required (MJ h^{-1})	15106	9168	3474
Thermal energy required (MJ h^{-1})[b]	30212	18337	6947
Pump energy requirement (MJ kg^{-1} butanol)[c]	6.0	3.7	1.4
Total process energy requirement (MJ kg^{-1} butanol)	15.7	13.4	11.1

[a] Refers to the amount of dissolved CO_2 in the pervaporation feed.
[b] Thermal energy = 2*Electrical energy.
[c] Total amount of butanol produced is 5000 kg/h.

4.4.2.2. Water treatment. Another factor that needs to be considered when doing the energy calculations is the treatment of the water streams for both the base case and the pervaporation-distillation process. For the base case, the proposed configuration, as shown in Fig. 10 a) (Section 4.2), contains an ultrafiltration unit to remove the solids which is sent back to the fermenter. However, unreacted acetic and butyric acid will end up in the water stream of the first water removal column (W−COL1, Fig. 11). Typically, the organics content (acetic and butyric acid) will be $\pm$ 0.4 wt.% and this stream will be sent to a waste water treatment facility to remove the residual organics [36,41].

In the case of the pervaporation-distillation process waste water will be produced if part of the recycle stream is purged due to a build-up of unreacted carbohydrates (*e.g.* xylose). The purge stream would consist of water, solvents as well as cells and unreacted carbohydrates. This stream could either be sent to a third fermenter to further convert the unreacted carbohydrates, in which case the products can be recycled into the process, or the stream could be sent to a waste water treatment facility. In the case of a waste stream, it will be sent to an end-of-pipe treatment facility for stillage. The treatment process involves physical separation (centrifuge) of the solids as well as evaporation and membrane separation. The energy consumption of this process varies greatly depending on the type of separation and the feedstock. From the recovered stillage other products can be produced such as animal feed, fertilizer and biological products such as enzymes, chitosan and plant hormones [42–45]. Alternatively, an ultrafiltration unit could be added to remove the solids from the purge stream and recycle it to the fermenter, this would however increase the capital costs of the process. The resulting stream could then be sent to a waste water treatment facility similar to the base case.

5. Conclusions

Experimental pervaporation experiments on a model fermentative ABE feed were performed and the results were used as input for Aspen Plus simulations. From the results of the simulations of various separation schemes it is concluded that the upstream addition of a pervaporation unit, to concentrate the organic feed, is energetically favourable. In addition, the pervaporation unit enables a liquid-liquid split of ABE into an aqueous and an organic fraction which are subsequently purified, which again saves energy for final purification. For the idealized case, where the presence of non-condensable gases in the permeate stream are not considered, the energy consumption reduces with $\pm$ 71% to 9.7 MJ kg^{-1} butanol as compared to a conventional distillation scheme, while still recovering industrial grade butanol. The energy consumption will increase depending on the amount of non-condensable gases in the permeate stream, as well as the energy cost for the treatment of potential waste water streams. For more realistic calculations it is seen that the energy consumption of the pervaporation distillation unit will increase with 6.0 MJ kg^{-1} butanol. The estimated energy consumption is then 15.7 MJ kg^{-1} butanol.

Acknowledgements

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