



A techno-economic comparison of various process options for the production of 1,1-diethoxy butane

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Abstract

BACKGROUND: Acetals can be considered important bio-based diesel additives. The production of most of these compounds, from an alcohol and an aldehyde, suffers from low conversion due to thermodynamic limitations. These limitations can be overcome through the removal of the by-product water. Previous studies showed that the *in situ* dehydration options of reactive distillation and pervaporation membrane reactor integration offer little advantage or at least not at reasonable unit dimensions. The aim of the present work is the development of a membrane based process and comparison with other alternatives (based on experimental data).

RESULTS: Three different membrane processes were developed. The one in which the reaction mixture is recycled over a first dehydration membrane module and subsequently through a simple distillation column, was found to give the highest overall conversion (100%) at low recycle rates and reasonable membrane area. This process was techno-economically compared with other possible alternatives: (1) a process based on a conventional tubular reactor and several distillation columns; and (2) a process based on reactive distillation.

CONCLUSIONS: Efficient water removal by membranes avoids possible azeotropes in downstream distillation units making them much simpler, reducing considerably the unit sizes and the energy demand (40% lower).

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Keywords: acetal; biodiesel; membrane separation; modeling; HybSi

NOTATION

A_m	Membrane area, m ²	R_v	Reactor volume, dm ³
A_t	Cross-sectional area, m ²	T	Temperature, C
C_i	Concentration of each compound, kmol m ⁻³	t	Time, h
CP_i	Specific heat for component i , kJ kmol ⁻¹ °C ⁻¹	v_s	Superficial velocity, m s ⁻¹
d_o	Membrane tube diameter, m	w	Catalyst loading in the reactor, kg m ⁻³
d_p	Catalyst particle diameter, m	x_i	Liquid molar fraction in the feed mixture
f_i	Flux through the membrane for component i , kmol m ⁻² h ⁻¹	y_i	Vapor molar fraction in the permeate mixture
F_i	Molar flow rate in the shell side for component i , kmol h ⁻¹	z	Normalized length (0...1)
J	Total flow through the membrane, kmol m ⁻² h ⁻¹	$\bar{\lambda}$	The latent heat of the permeating fluid, kJ kmol ⁻¹
k_1	Kinetic constant for the forward reaction, (m ³) ³ /(kmol ² ·s·kgcat)	ΔH_r^{298K}	Enthalpy of reaction at 25 °C, kJ mol ⁻¹
k_2	Kinetic constant for the reversible reaction, (m ³) ² /(kmol·s·kgcat)	γ_i	Activity coefficient for component i
L	Reactor length, m	ε	Void fraction
N	Number of membrane tubes	μ	Dynamic viscosity of the liquid in the feed-retentate side, Pa s
P_F	Pressure in the feed side, bar		
p_m	Perimeter of total membrane tubes, m		
P_p	Permeate pressure, bar		
p_i^{sat}	Saturation pressure of component i , bar		
Q_i	Permeance of component i , kmol m ⁻² h ⁻¹ bar ⁻¹)		
Re	Reynolds number		

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ρ	Density of the liquid on the feed-retentate side, kg m^{-3}
Φ	Sphericity of particles ($\Phi = 1$ for perfect sphere)
χ	Reactor conversion of 1,1-diethoxy butane, %
θ	Water cut – water in permeate divided to the water coming with the feed, %
ν_i	Stoichiometric coefficient (negative for reactants)
ν	Volumetric flow, $\text{m}^3 \text{h}^{-1}$
H10X	Heat exchanger
M10X	Mixer
P10X	Pump
PV100	Pervaporation module
RD-T100	Reactive distillation column
S100	Splitter
T10X	Distillation column
V100	Decanter

INTRODUCTION

Acetals are promising bio-based diesel additives.¹ The miscibility of these oxygenated compounds with (bio)diesel is satisfactory, and the emission of particulate matter and nitrogen oxides, NO_x , can be lower using them as diesel additives. A light acetal as 1,1 diethoxy ethane has a flash point of -21°C , which is much lower than the required value of 55°C . 1,1-diethoxy butane, a heavier acetal, fulfills all diesel specifications. It can be produced from ethanol and butanal and both can be obtained directly or indirectly from renewable feedstock via fermentation. Ethanol is a direct product of fermentation and butanal can be obtained from dehydrogenation or partial oxidation of n-butanol, which can also be a direct product of fermentation.

The synthesis of acetals typically occurs in a homogeneously catalyzed media in the presence of mineral acids such as H_2SO_4 , HF, HCl or p-toluene sulphonic acid.^{2–4} The intrinsic disadvantages of these catalysts are their corrosive nature and negative environmental effects. This has led to the study of alternative solid acid catalyst, and it is concluded that ion exchange resins show better performance than other catalysts.¹

In recent years, there has been an increasing interest in process intensification. An example is the development of advanced processes where reaction and separation are combined in one single unit. These systems can overcome the thermodynamically limited equilibrium conversions that are typical for esterification or acetalization reactions.^{1,5–8} If water is a by-product, dehydration membrane reactors are among the most promising alternatives in this kind of reaction. The continuous *in situ* water removal from the reaction mixture shifts the reaction towards product formation.^{9–15} Saracco and Specchia,¹⁶ Coronas and Santamaría¹⁷ and Sanchez Marcano and Tsotsis¹⁸ were among the first to describe the advantages of a membrane reactor for different applications. More recently Drioli and Giorno¹⁹ have published an extensive work on membrane phenomena including state-of-the-art on pervaporation membrane reactors.

The focus of most publications on this topic is lab scale batch studies and their modeling.^{14,15,20–24} However, some authors have studied different continuous processes. Zhu *et al.*⁹ performed continuous pervaporation experiments in a tubular pervaporation membrane reactor, and modeled esterification reactions using H_2SO_4 as a homogenous catalyst. De la Iglesia *et al.*²⁵ also performed esterification reaction experiments in a continuous tubular reactor. Amberlyst 15 was used as catalyst,

placed inside the membrane. Lim *et al.*¹¹ studied different process configurations, and concluded that tubular membrane reactors lead to a better performance than stirred tank membrane reactors. Nemeč *et al.*²⁶ analyzed multifunctional tubular reactors with the catalyst particles in the annular region between the membrane and the module shell, and their results were not very promising.

Some time ago investigations of the different possibilities of 1,1-diethoxy butane (acetal) production at industrial scale were started. The first approach was by reactive distillation. It was found that thermodynamic limitations could be overcome, but due to the small volatility differences among the compounds the final conversions achieved were not as high as was desired.²⁷ More recently, the development of membrane-based separation of water from the reaction mixture²⁸ was considered. Different types of dehydration membranes can be used in the acetalization reaction for water removal. Many polymeric dehydration membranes show high separation factors (polyamide, chitosan, polyimide based membranes)²⁹ but they offer really low fluxes. Other inorganic membranes like Pervatech amorphous silica membranes show high fluxes but long-term stability could be an issue.³⁰ For this reason a hybrid inorganic–organic membrane (HybSi) was chosen for this application, having good separation factors and acceptable fluxes. HybSi is an organic–inorganic hybrid silica-based amorphous material. The hybrid nature of this material lies in the fact that each silicon atom is not only connected to oxygen atoms as in pure silica, but also to an organic fragment. The special feature of HybSi is that the organic fragments act as integral bridging fragments of the structure, and not just as end standing groups as in methylated silica. The result is a true hybrid silica pore network in which organic and inorganic fragments cooperate. More information can be found in an earlier report³¹ and at www.hybsi.com.

It was shown that in a batch membrane reactor, conversions are much higher than the thermodynamically-limited equilibrium conversion. These experiments have shown the feasibility of this approach, and this is a prime requirement for a viable process. However, the conclusion was that an integrated pervaporation membrane reactor using an Amberlyst catalyst and dehydration membranes was unlikely to be economically attractive because of the required unrealistic catalyst volume to membrane area ratio.³² In the current paper various new and alternative non-integrated methods of combining reaction and membrane separation are discussed, including setting up and discussing new possible flowsheets of the integrated process that could lead to a better process. Further, a techno-economic comparison between the best membrane-based alternative, the conventional, and a reactive distillation process is made.

APPROACH

The work starts with a membrane reactor case to identify and select the configuration with the highest conversion and lowest membrane area. The following scheme with uncoupled separation and reaction is evaluated first and compared with a combined reactor and membrane process:

- 1) Reactor followed by pervaporation in series
- 2) Reactor and pervaporation with a recycling loop
- 3) Reactor followed by pervaporation and distillation with a recycling loop

To keep consistency with previous studies on semi-pilot experiments on reactive distillation,²⁷ a fixed flow rate of 7 L h^{-1} is

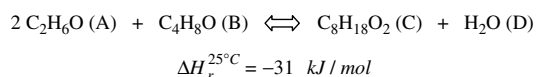
considered. Further, the best resulting membrane-based configuration will be used for scale-up to an industrial scale and a techno-economic evaluation comparison with other technologies (a reaction + distillation case and a reactive distillation case) is made. The comparison is based on calculated conversion, required membrane area, sizing of unit operations, and costing, all of these calculated based on the estimated material and energy balances.

All the required kinetic data for the reaction were obtained experimentally.³³ The component permeance data through the membrane were obtained from ethanol/butanol/1,1-diethoxy butane/water batch dehydration experiments, and validated using a batch model.²⁸ All these data were used to model a water dehydration membrane module and a tubular reactor in Aspen Custom Modeler including their design aspects. These custom models were used afterwards as add-ins in Aspen Plus for detailed process calculations and evaluation.

GOVERNING EQUATIONS

Reaction kinetics

The reaction under consideration is the acetalization of ethanol (A) and butanal (B) to produce 1,1-diethoxy butane (C) and water (D):



Like most of the acetalization reactions, this reaction is exothermic with low equilibrium conversions to 1,1-diethoxy butane, typically in range of 40 to 50% between 40 and 60 °C.³³ The equilibrium conversion is higher at lower temperatures while pressure has no or only minor influence on the conversion. Acidic ion exchange resins catalyze the reaction and a pseudo-homogeneous kinetic model (Equation (1)) can describe accurately the reaction progress.

$$\frac{dC_i}{dt} = (v_i w k_1 C_A^2 C_B - v_i w k_2 C_C C_D) \cdot 3600 \quad (1)$$

For all simulations conventional plug flow tubular reactors were used with the following design equation:

$$\frac{dF_i}{dz} = L A_t \left(v_i w k_1 F_A^2 F_B \frac{1}{V^3} + v_i w k_2 F_C F_D \frac{1}{V^2} \right) \cdot 3600 \quad (2)$$

Membrane transport

The transport equation for a certain component through the membrane is described by Fick's Law, given by the relation^{34,35}

$$f_i = Q_i (x_i \gamma_i P_i^{\text{sat}} - y_i P^{\text{perm}}) \quad (3)$$

The saturation pressure P_i^{sat} of each component was calculated with Antoine's equations.³⁶ Activity coefficients were calculated with the UNIFAC thermodynamic model for ethanol/butanol/1,1-diethoxy butane/water mixtures. This method has been used, as consistent VLE data of 1,1-diethoxy butane with other components are not available in the open literature. For these cases, UNIFAC is the recommended method and a more detailed discussion on this topic is provided by Prausnitz.³⁶ This relation (3) shows that the pressure on the feed side of the membrane has no effect on the flux, while the temperature influences the saturation pressure, and therefore the flux across the membrane. At higher temperatures

the saturation pressure in relation (3) increases and thus the fluxes are higher, and this leads to a lower membrane area required for the separation. Previously, the validity of using an Arrhenius type equation to describe the permeance values was confirmed, and the corresponding activation energies can be obtained by fitting experimental data within the conditions under study in the present work.²⁸

Pervaporation module modeling

A multi-tubular pervaporation module was chosen to simulate the water removal from the mixture. This design is similar to shell and tube heat exchangers, where membrane tubes replace the pipes through which the heat transfer occurs. The following assumptions are made in the modeling of such a pervaporation module:

- The selective membrane layer is on the outside (shell side) of the membrane tube.
- The membrane is inert and does not influence the reaction.
- Concentration-polarization and temperature-polarization are negligible.
- The permeate side is perfectly mixed.
- Permeance values depend only on the temperature, and not on the composition of the mixture.

Based on the above assumptions, the governing equations of multi-tubular pervaporation module are given by relations (4) and (5). These relations account for the mass balance for each component (4) and the energy balance (5).

$$\frac{dF_i}{dz} = -L f_i p_m \quad (4)$$

The pervaporation module was operated as an adiabatic system, which is at an industrial scale more common than isothermal systems. The evaporation during pervaporation requires energy and reduces the feed temperature. For these reason an energy balance is required in order to get the temperature profile along the pervaporation module (5).

$$\frac{dT}{dz} = \frac{-L N \pi d_0 (J |\bar{\lambda}_i(T)|)}{\sum (F_i C_{p,i})} \quad (5)$$

The pressure drop was considered negligible in the pervaporation module. In the case of tubular reactors, the pressure drop through the packed catalyst beds was accounted for through the Ergun equation:

$$\frac{dP_F}{dz} = L \left[\frac{150 \mu (1 - \varepsilon)^2 v_s}{\phi \varepsilon^3 d_p^2} + \frac{1.75 (1 - \varepsilon) v_s^2 \rho}{\phi \varepsilon^3 d_p} \right] \cdot 10^{-5} \quad (6)$$

Hydrodynamics

In the current model, concentration and temperature polarization effects are not taken into account. The validity of these assumptions has been proven by the batch reactor analyses. Comparison between experimental data and modeling predictions showed fairly good agreement.²⁸ This is in agreement with the findings by Sommer³⁷ who found a limited influence of polarization effects. The origin of the concentration polarization can be found in the selective transport of water through the membrane. As a result the water may be depleted from the bulk towards the membrane.³⁷ Temperature polarization is a

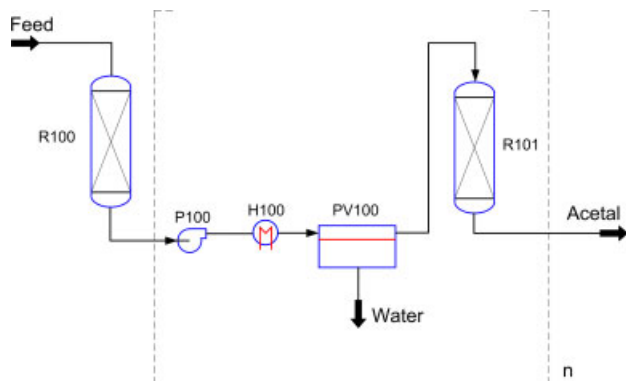


Figure 1. Flow sheet diagram of PFR and PV modules in series.

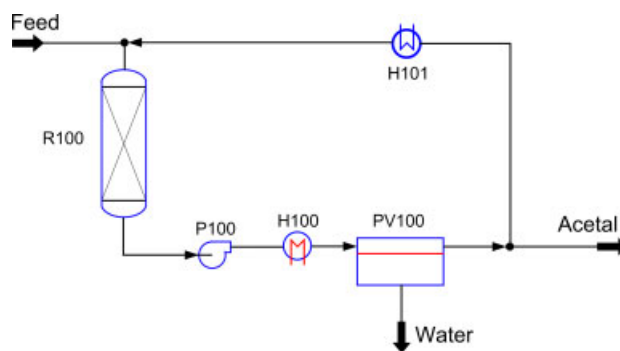


Figure 2. Flow sheet diagram of reactor and pervaporation with recycling loop.

consequence of the evaporation that occurs over the membrane. The necessary vaporization enthalpy is taken from the energy of bulk fluid on the feed/retentate side decreasing the mixture temperature towards the membrane surface. Further precautions have been taken to limit the possible effects. In a laminar flow regime and at high membrane permeances polarization effects can be significant resulting in decreased pervaporation efficiency. Sommer *et al.*³⁷ concluded that, for an annular duct module type, there is a steep efficiency increase at Reynolds = 2300 (transition between laminar and turbulent flow regime). For this reason the feed will be kept in the transition flow regime throughout the current study. In our case, this means that the actual module efficiency is ~90%, leading to an acceptable small underestimation of the membrane area needed. In the present case, as a multi-tube module was considered the transition flow regime limits are between $Re = 20$ and 100 .^{38,39} In these cases the outer diameter of the membrane tubes must be used for Re calculations

$$Re = \frac{d_0 v \rho}{\mu} \quad (7)$$

The module design was based on the shell-and-tube heat exchangers using the equilateral triangular layout, the one that offers the highest membrane area to volume ratio. The typical pitch distance of 1.25 times the pipe diameter³⁸ was used. Thus, the membrane module used to treat a feed flow rate of 7 L h^{-1} was based on 43 tubes with a diameter of 3 mm and a module shell diameter of 30 mm, as the most promising configuration.

UN-COUPLED PROCESS ALTERNATIVES

Based upon the process analysis, three different process designs based on adiabatic tubular reactors and adiabatic pervaporation modules have been set up and evaluated:

- i) reactor and pervaporation in series (Fig. 1);
- ii) reactor and pervaporation including a recycle loop (Fig. 2);
- iii) reactor, pervaporation and a distillation column recycling the top stream of the distillation (Fig. 3).

In these cases no catalyst particles are present between the membrane tubes as the reactor and membrane separator are physically separated. As a result, the ratio between the membrane area and the shell side volume can be much higher and the water removal by pervaporation is more efficient than in the case of a multi-tube plug flow membrane reactor (MPFMR). A detailed analysis of the three configurations using Aspen flow sheeting will be presented.

Reactor and pervaporation in series

Initially the optimum number of adiabatic plug flow reactors (PFR) and pervaporation modules (PV) placed in series as shown in Fig. 1 was estimated. The feed of the first reactor was set at 25°C . After each reactor a liquid pump was placed to compensate for the pressure drop in the reactor. This was followed by a heat exchanger to increase the inlet temperature of the mixture to the pervaporation unit to its boiling point of around 80°C . During the pervaporation operation the temperature decreased and the cooled retentate stream was led to the next reactor. It should be noted that a lower temperature leads to higher conversions and is thus beneficial for the following reactor. The membrane area of each pervaporation module was optimized. For that purpose the module length was varied keeping the module diameter constant and membrane configuration as explained earlier in order to have a suitable flow regime. The module length was chosen after observing the decreasing curve of the driving force in each case. The main results are presented in Table 1.

Table 1 shows that the conversion increases with the number of reactors/pervaporators in series. With five PFR reactors and four PV modules ($n = 4$) and a total membrane area of 1 m^2 in series, the achieved maximum conversion was 71.2%, which is comparable with the experimental conversions achieved in semi-batch mode.²⁸ However, the increase in the conversion after three reactors is limited and it does not make sense to have more than four PV modules. Based upon these results some observations can be made:

- The first PV100 module was much larger than the other modules; the value for A_m reduces from 0.45 m^2 for the first PV module to 0.10 m^2 for the fourth module. The reason is that in the first module a large amount of water had to be separated resulting in a large temperature drop, reducing the driving force at the end of the module and thus the flux. Higher water outlet content would give a lower membrane area but could lead to limitations for R101.
- The inlet temperature in the reactors R103 and R104 was rather high and a small cooler could improve the conversion of this reactor. This cooler could be heat integrated with a heat exchanger H100n. This could also lead to lower operating costs.
- The ethanol to butanal feed ratio in the first reactor was the stoichiometric ratio of 2:1. In the other reactors this ratio gradually decreases as some ethanol permeates through the membrane. Adding some extra ethanol, e.g. before reactor R103, would help shift the equilibrium further.

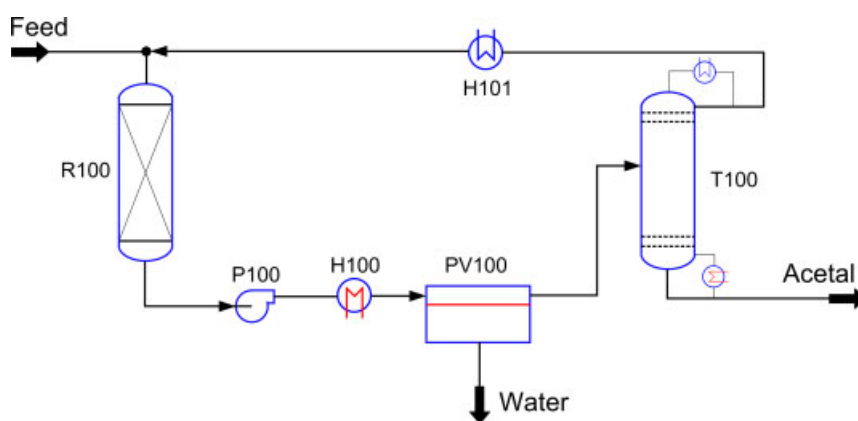


Figure 3. Flow sheet diagram of the process including a distillation column and a recycle loop.

Table 1. Process parameters in each unit. 'Reactor and pervaporation in series' configuration									
	R100/PV100		R101/PV101		R102/PV102		R103/PV103		R104
R_V , dm ³ /A _m , m ² (reactor vol./mem. area)	0.053/0.45		0.088/0.24		0.044/0.20		0.027/0.10		0.008
X %/ θ , % (conversion/water cut)	45.8/85.8		60.3/92.4		66.3/93.6		69.3/91.2		71.2
Re range	13–21/14–28		13–16/18–26		17–18/21–25		19–20/22–25		19–20
T_{in} , °C	25/76.6		33.1/78.6		54.0/81.4		69.7/83.1		76.8
T_{out} , °C	60.7/33.1		46.5/54.0		59.9/69.7		72.8/76.8		78.8
Outlet composition, mol fr.									
ethanol	0.433	0.505	0.397	0.430	0.376	0.377	0.347	0.342	0.322
butanal	0.211	0.252	0.197	0.222	0.195	0.208	0.193	0.201	0.191
acetal	0.178	0.213	0.301	0.339	0.385	0.411	0.438	0.455	0.473
water	0.178	0.030	0.105	0.009	0.044	0.003	0.022	0.002	0.014

The maximum conversion is about 71%, which is much higher than the equilibrium conversion of 38%. The reason that the conversion does not increase to, say, 90% is the fact that the acetal concentration is increasing further and further in each step thus limiting the equilibrium of the reactor. In the end this configuration thus shows a similar performance to a batch reactor. The advantage of this configuration, when compared with combined reactor and separator in one unit,³² is a more suitable catalyst to membrane area ratio, a more flexible design and a lower pressure drop. In the membrane reactor of combined reaction and separation, the presence of catalyst particles between membrane tubes leads to large separation distances between membrane tubes in order to avoid wall effects and therefore unrealistic unit dimensions. However, in both cases the flow regime was the same, always above the laminar flow regime limit. The configuration in series leads to a shorter reactor and pervaporation membrane to achieve the same conversion (Table 2). However, this configuration is complex and a large number of units (five reactors and four pervaporation modules) are required.

Reactor and pervaporation with a recycle loop

To reduce the number of units, a process with a recycle loop was considered. In this case only one reactor and one pervaporation module are required. It is anticipated that this would lead to lower capital expenditure. Figure 2 shows this basic process configuration.

For this configuration the influence of the recycle ratio on the reactor length and the PV module length was determined.

Table 2. Sizes for unit operations in series and for MPFMR		
Dimension	PFR+PV in series	MPFMR ²⁸
Reactor length/PV module length (m)	1.3/2.45	15
Reactor diameter/PV module diameter (mm)	15/30	22
Catalyst volume (dm ³)	0.23	3.39
Total membrane area (m ²)	1	0.66

By increasing the recycle ratio, this being the ratio between the recycle molar flow and the retentate molar flow, the flow rate in the reactor increases. Thus, the residence time decreases and longer reactors and membrane modules are required in order to end up with the same water cut (θ) and conversion values as in the previous case. In addition, also the plug flow reactor diameter to length ratio was modified for each recycle ratio in order to avoid extremely high pressure drops.

The simulations show that conversions of 65–68% can be reached at a very high recycle ratio of 0.8–0.9. At high recycle ratios, the flow and the Re numbers in the reactor and pervaporation module increase rapidly and the diameter/length ratio was varied to keep the simulations in similar flow regimes. As a result these units become larger. The shell diameter of the pervaporation module had to be increased from 0.03 to 0.07 m. At the same time the membrane area increased to 1.6 m² to achieve 71% conversion. This value is also comparable with

the maximum conversion achieved experimentally in a batch membrane reactor.²⁸

Reactor, pervaporation and distillation with a recycle of the top stream

Both configurations presented above require a relatively large membrane surface area to fulfill all the hydrodynamic constraints and to achieve high conversion. In an attempt to reduce this, a last process configuration was designed in which the splitter of the previous process was replaced by a distillation column. The use of a distillation column will lead to higher operating and capital costs because of the energy demand of the reboiler and the higher investment in the column compared with a simple splitter. An economic benefit is still anticipated, as only the non-reacted reactants are recycled to the reactor and an overall conversion of 100% can be achieved. Pure acetal leaves the column at the bottom. As result the concentration of the reactants will be higher and overall conversion of 1,1-diethoxy butane will increase. In addition, the flow rate through the system will be lower and this will lead to smaller equipment. The process configuration is shown in Fig. 3.

As before and for the same reasons, a liquid pump and a heat exchanger are placed between the reactor and the pervaporation module. This arrangement ensures optimal utilization of the membrane at minimum surface area. Thus, the required membrane area is 0.81 m², 20% and 50% less than in the previously explained options.

The added value of this arrangement is that the absence of water simplifies the distillation process dramatically. For the separation of acetal via distillation from ethanol and butanal only six theoretical trays (incl. condenser and reboiler) are required to reach 99.99 mol% purity and a recovery of 99%. When water is not removed prior to the distillation, a complex process with at least two columns and with many trays is required. This can be attributed to the existence of azeotropes that water forms with all components. Table 3a and 3b presents the main dimensions and results of the calculations. The number of stages and the feed stage of the simple distillation column presented in Table 3b was found minimizing the reboiler (and condenser) heat duties for the above mentioned specifications. A tray efficiency of 0.6 was applied.

Selection of the most promising alternative

Comparison of the three process schemes and the multi-tube plug flow membrane reactor (MPFMR) (Table 4), shows that the removal of water alone either by a series or recycle system leads to conversions similar to those observed experimentally in a batch system.²⁸ These configurations require a relatively large membrane area or an unrealistic design. The membrane reactor (MPFMR) requires the least membrane area but due to the design constraints generated by the presence of the catalyst, the length of the reactor to treat 7 L h⁻¹ is unrealistic.³² The last configuration in which almost pure ethanol and butanal is recycled results in a process conversion of almost 100%. This high conversion is anticipated to compensate for the additional energy requirement of the distillation column. Anyhow, the series and recycle loop options do need extra (downstream) separation as the acetal is not pure. Also the required membrane surface area of 0.81 m² is anticipated to be reasonable. On the basis of these considerations the configuration of a tubular reactor, a pervaporation module and a distillation column was selected for more detailed evaluation and comparison with the base case process and a reactive distillation process.

Table 3a. Process parameters in the reactor and pervaporation module (see Fig. 3). 'Reactor, pervaporation and distillation' process configuration

Reactor (R100)		Pervaporation unit (PV100)	
Inlet flow, L h ^{-1a}	15.9	Inlet flow L h ⁻¹	15.9
Inlet molar flow rate, kmol h ⁻¹	0.17	Inlet molar flow rate, kmol h ⁻¹	0.15
Re range	11–17	Re range	40–0
T _{in} /T _{out} , °C	25/58	T _{in} /T _{out} , °C	80/36
Volume, dm ³	0.12	Membrane area, m ²	0.81
χ, %	43.5	θ, %	79.4
		Permeate pressure, mbar	5
Outlet comp, mol fr.		Outlet comp, mol fr.	
Ethanol	0.167	Ethanol	0.200
Butanal	0.208	Butanal	0.249
Acetal	0.424	Acetal	0.501
Water	0.201	Water	0.050

^a Inlet flow = fresh feed flow + recycle flow

Table 3b. Process parameters in the distillation column (see Fig. 3). 'Reactor, pervaporation and distillation' process configuration

Distillation column (T100)		
Condenser duty, kW		-1.73
Reboiler duty, kW		2.23
Real stages (incl. reb. & cond.)		13
Feed stage*		9
Recycle ratio		0.22
Distillate to feed molar ratio		0.81
Temperature top/bottom, °C		74.1/119.5
Inlet molar flow rate, kmol h ⁻¹		0.12
	Top	Bottom
Outlet molar flow rate, kmol h ⁻¹	0.10	0.02
Outlet comp., mol fr.		
Ethanol	0.620	0
Butanal	0.309	0
Acetal	0.010	0.999
Water	0.061	0.001

* The head of the column, the condenser, is considered the first stage.

FULL-SCALE PROCESS COMPARISON

In the above section it is shown that the use of dehydration membranes can facilitate the acetal production process. However, it is necessary to know if this process can compete with other alternatives, from the economic point of view. Therefore, in this section three conceptual process designs for a full-scale industrial acetal production process are compared:

- conventional tubular reactor followed by a distillation train (base case);
- reactive distillation;
- conventional tubular reactor followed by a pervaporation step and a distillation column.

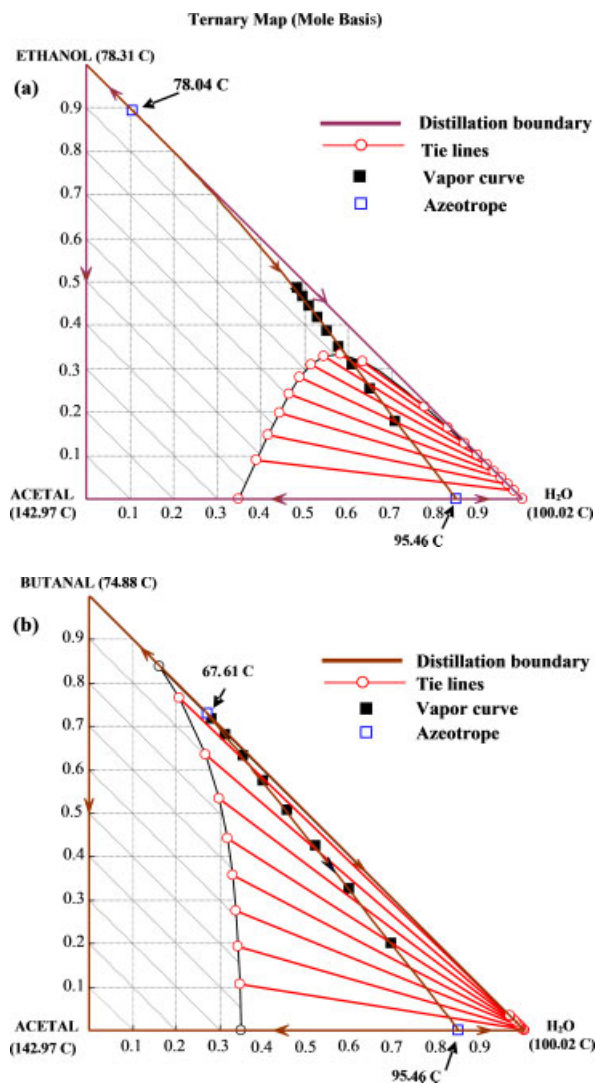
With the information gathered in the process development simulations (material and energy balances) the different unit

Table 4. Comparison of the developed processes with membranes (treated fresh feed: 7 L h⁻¹)

Process configuration	Conversion (%)	Membrane tubes length (m)	Membrane area (m ²)	Catalyst volume (dm ³)
MPFMR ²⁸	74.6	15	0.66	3.39
PFR + PV in series	70.6	2.45	1.00	0.22
PFR + PV + recycle	71.0	0.6	1.60	2.39
PFR + PV + Dist	99.7	2	0.81	0.12

Table 5. Azeotropes formed in the quaternary mixture. ^a Estimated by Aspen, ^b Kirk Othmer Encyclopedia⁴⁰

Azeo. no.	Azeo. type	EtOH	Butanal	Acetal	Water	T _{boil}
		mol %				°C
1 ^a	homogeneous	26.2	73.8	0	0	72.5
2 ^a	homogeneous	89.3	0	0	10.7	78.0
3 ^a	heterogeneous	0	72.8	0	27.2	67.6
4 ^a	heterogeneous	0	0	14.7	85.3	95.6
5 ^b	heterogeneous	12.9	60.1	0	27.0	67.2

**Figure 4.** Vapor-liquid-liquid equilibrium diagrams for (a) ethanol-acetal-water and (b) butanal-acetal-water ternary mixtures estimated by Aspen Plus.

operations are dimensioned and capital and operating costs estimated. This comparison allows for the selection of the process with the lowest costs. In all cases the production amount of acetal is set at 50 kt acetal year⁻¹; this is a typical plant capacity and is comparable with the average size of an ETBE production plant. The acetal purity is set at 99.99 mol% for each case.

Base case

The base case consists of a 1,1-diethoxy butane production process based on conventional unit operations currently used in the process industry and is built up from a tubular reactor and conventional distillation. The conceptual design of a process requires the knowledge of the thermodynamic behavior of the system, and the appropriate system configuration is determined. Since the distillation is the separation unit, it is important to know the vapor-liquid equilibrium behavior of the components present. These diagrams, generated by Aspen Properties using UNIFAC thermodynamic package, are presented in Fig. 4, and the list of azeotropes formed is given in Table 5. In the system four azeotropes can be identified and in some regions of the ternary diagram, two liquid phases are formed.

Doherty and Malone⁴¹ is an excellent reference to the systematic design of a conceptual process flow diagram. Following the explanation in the book the process flow diagram presented in Fig. 5 was obtained. The conventional tubular reactor is followed by two distillation columns with a liquid-liquid decanter in between. The aim of the first distillation column (T100) is to remove water and acetal from the bottom. Acetal being less volatile than water will be concentrated in the bottom while butanal being more volatile than ethanol is collected at the top of the column. However, the ethanol/water azeotrope will limit this separation and part of the water will go to the top and will be recycled to the reactor. Therefore, the selected design specification for this column is ethanol recovery in the top, which is set to 0.9999 mol mol⁻¹, so the acetal stream will not contain any ethanol. The second design specification is for water recovery at the bottom, which is set to 0.5 mol mol⁻¹ and is limited by the ethanol/water azeotrope.

A ~50/50 mol% of water and acetal mixture leaves the bottom of T100 at 90 °C. Under these conditions, two liquid phases are formed, Fig. 6. The aqueous phase is nearly 100% pure water. This thermodynamic feature of the mixture is used to separate water in decanter V100. The organic phase, containing ~35% water, is dehydrated in T101. Acetal, 99.99% purity, is removed as product from the bottom while the top stream with near to azeotropic composition, 14.7 mol% acetal, is recycled back to the decanter V100. The allowable acetal content in this top stream is set at 20 mol%. This value is near the azeotropic composition but sufficiently far away from it to avoid high reboiler (and condenser) duties. To prevent the decomposition of 1,1-diethoxy butane to 1-ethoxy-1-butene and ethanol at high reboiler temperatures,²⁷ the column T101 was operated at sub-atmospheric pressure of 0.5 bar.

The design specifications of the industrial scale conventional process and main calculated equipment data are summarized in Table 6.

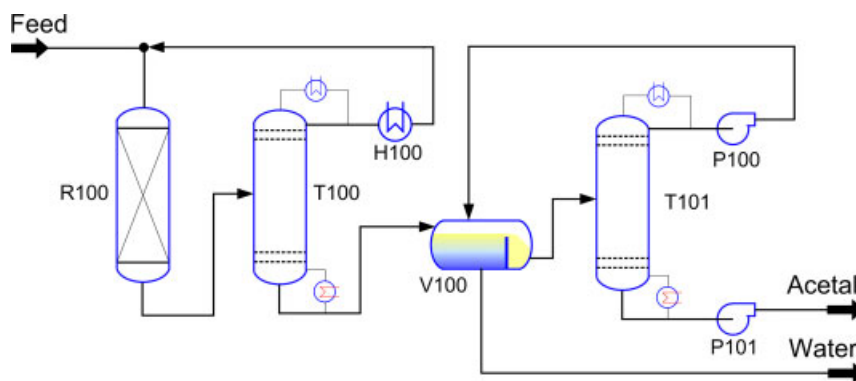


Figure 5. Process flow sheet diagram of the conventional process or the 'base case'.

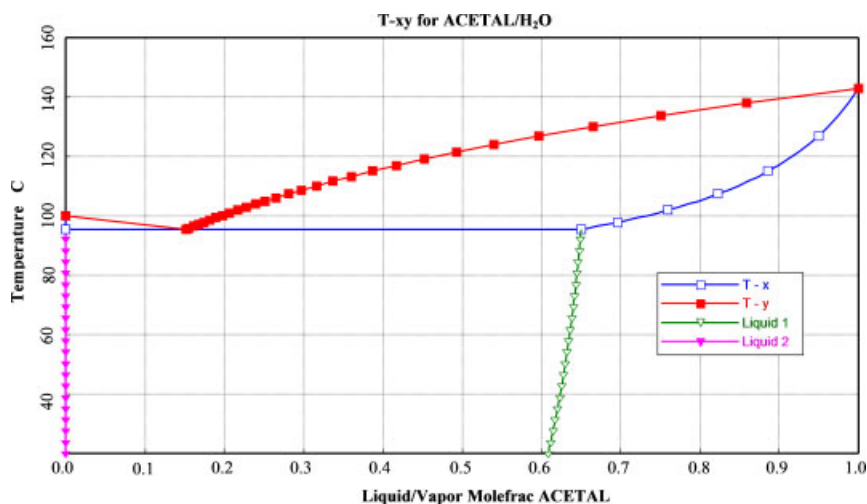


Figure 6. Vapor-liquid-liquid equilibrium of 1,1-diethoxy butane/water.

	Distil. Column 1 (T100)	Distil. Column 2 (T101)
H ₂ O recovery in the bottom, mol mol ⁻¹	0.5	-
EtOH recovery in the top, mol mol ⁻¹	0.9999	-
Acetal purity in the bottom, mol mol ⁻¹	-	0.9999
H ₂ O composition top, mol mol ⁻¹	-	0.8
Equilibrium stages (reb & cond. included)	50	11
Real stages (reb & cond. included)	82	17
Feed stage	17	6
Reflux ratio	1.15	0.5
Reboiler duty, MW	5.85	0.73
Condenser duty, MW	5.52	0.61
Bottom to feed ratio	0.26	0.56
Pressure (column head), bar	1	0.5
Column diameter, m	1.75	1
Column height, m	51	10

* The reactor and the decanter operate in adiabatic regime.

51 m height of the first distillation column is within the limit of realistic column dimensions.⁴²

Reactive distillation case

Reactive distillation has been proven to overcome thermodynamic limitations and conversions higher than those at equilibrium can be achieved.²⁷ Still, the conversion is not complete and an additional separation train was developed to reach 99.99% product purity. The flowsheet diagram (Fig. 7) was based on the same thermodynamic property method and design constrains as in the conventional case.

The reactive distillation column configuration that meets the design constraints was found experimentally and by modeling²⁷ and applied in Aspen Plus. Similar to the base case, two additional columns were required in addition to the reactive distillation column to reach the purity demands. The maximum achievable conversion in the reactive distillation unit itself is 50%²⁷ but as some water is recycled the step conversion decreases to 43%. The step conversion in the tubular reactor of the base case was 39%. The conversion increase using reactive distillation is thus minimal. The main reason for this small difference can be found in the higher operating temperature of the reactive distillation column. In the base case, the inlet and outlet temperature to the reactor are at 25 °C and 56 °C, respectively. In a reactive distillation system the reaction temperature is given by the reboiler composition and therefore, reboiler temperature, being in this case ~73 °C.

The product yield is for this base case the highest achievable, as no reactants are lost in the product or in the by-product streams. Consequently, the overall conversion is nearly 100%. Further, the

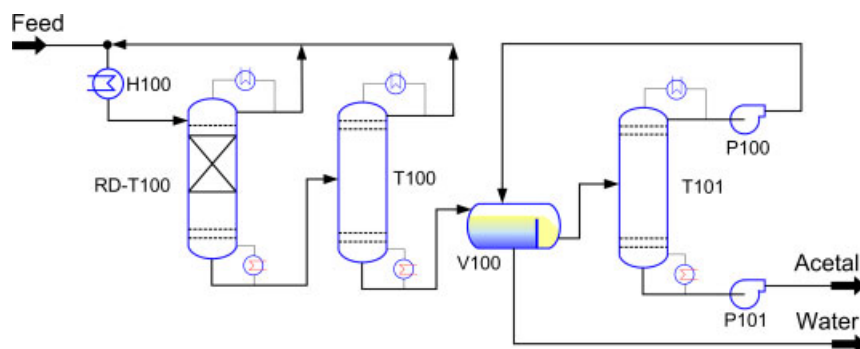


Figure 7. Process flow diagram of the reactive distillation case.

Table 7. Design specifications and calculated data for reactive distillation case

	Reactive dist. column (RD-T100)	Dist. Column 1 (T100)	Dist. Column 2 (T101)
H ₂ O recovery bottoms, mol mol ⁻¹	–	0.8	–
EtOH recovery top, mol mol ⁻¹	–	0.9999	–
Acetal purity in the bottoms, mol mol ⁻¹	–	–	0.9999
H ₂ O composition top, mol mol ⁻¹	–	–	0.8
Equilibrium stages (reb & cond. Included)	8	50	11
Real stages (reb & cond. Included)	12	82	17
Feed stage	2	7	6
Reflux ratio	5	5.98	0.5
Reboiler duty, MW	8.33	4.85	0.73
Condenser duty, MW	8.62	4.84	0.61
Bottom to feed ratio	0.45	0.58	0.56
Pressure (column head), bar	1	1	0.5
Column diameter, m	2	1.6	1
Column height, m	10	51	10

* The decanter was considered as an adiabatic unit.

Since the reaction is exothermic, the conversion is lower at higher temperatures.

Table 7 shows the main specifications and calculated data for the reactive distillation case. It is remarkable that the utilization of a reactive distillation column does not lead to a significant change of the unit size compared with the base case. This is likely to be related to the existing azeotrope between water and ethanol.

Membrane case

The first estimations indicated that for the process option where a tubular reactor, a pervaporation module, and a distillation column are combined, Fig. 3, about 1200 m² of membrane area is required in order to produce 50 kt acetal year⁻¹ and have 5 mol% of water in the retentate. This amount of membrane area seems to be very high and will lead to unacceptable capital, maintenance, and membrane replacement costs. In addition, a temperature decrease

of ~45 °C between the inlet and the outlet of the pervaporation module, Table 3a, indicates that the dehydration process could benefit from the use of an isothermal pervaporation module. Under isothermal operation at 80 °C, while keeping the permeate composition unchanged, the required membrane surface area decreases from 1200 m² to 546 m². In all cases the permeate pressure was kept equal to 5 mbar. To maintain the isothermal operation, an additional energy (e.g. steam) of 0.5 MW is required. However, the price of this energy is much lower than the cost savings made due to the reduction of the membrane area. Further cost reductions are expected as it is very possible that heat of low exergetic quality is available on site of the prospective plant.

One limitation of the present process is the loss of ethanol through the membrane to the permeate side, ~6 mol%. In practice various alternatives to recover the small amount of ethanol can be designed, including a recycle to the rectifier of the ethanol production process. In order to keep the design boundary conditions the same as in the previous processes, an additional ethanol/water distillation column has been included in the current study. This recovered ethanol containing 25 mol% water is recycled to the reactor. A high composition of water, which is far from the azeotropic composition, is deliberately selected to ensure that this distillation is easy and cheap. This part of the process (not shown in Fig. 3) has been taken into account in the economic evaluation of this case. The design specifications and calculated results of distillation columns of this process case are shown in Table 8.

In this last case, the substitution of one distillation column by a dehydration membrane module leads to a lower energy consumption than in the base case and the reactive distillation case. Moreover, the efficient water removal through the membranes make the downstream distillation process much easier since water forms an azeotrope with every component (see Table 5).

Preliminary cost evaluation

To estimate capital expenditure for building the presented alternatives, each piece of equipment is sized using the information given in the previous process calculations. The *Chemical Engineering Plant Cost Index (CEPCI)* value given at the end of 2009 (511.8) is used and the accuracy of the estimation is around ±25%. The corrosive nature of aldehydes prescribes the use of stainless steel⁴² and this material was selected for all parts. The Total Capital Investment evaluation is based on the bare module technique, with cost equations and bare module factors as presented by Turton *et al.*⁴² For that purpose, the CAPCOST tool developed by Turton *et al.*⁴² has been used. The price of the membrane has been estimated based on Mitsui Zeolite A membrane system cost⁴³ which was combined

Table 8a. Design specifications and calculated data for membrane case (reactor + pervaporation module + distillation unit)

	Dist. Column T100	EtOH recovery column
Acetal recovery bottoms, mol mol ⁻¹	0.9999	–
Acetal purity in the bottoms, mol mol ⁻¹	0.9999	–
EtOH composition top, mol mol ⁻¹	–	0.75
H ₂ O composition bottom, mol mol ⁻¹	–	0.999
Equilibrium stages (incl. reb & cond.)	15	9
Feed stage	10	7
Reflux ratio	0.72	3.3
Reboiler duty, MW	3.34	0.27
Condenser duty, MW	3.38	0.16
Bottom to feed ratio	0.19	0.93
Pressure (column head), bar	0.5	1
Column diameter, m	2.1	0.3
Column height, m	16	8

* The design specification in the pervaporation module was 5% water (mol) in the retentate

Table 8b. Process parameters in the reactor and pervaporation module (see Fig. 3). 'membrane case' (reactor + pervaporation module + distillation unit)

Reactor data (R100)		Pervaporation Data (PV100)	
Inlet flow, m ³ h ⁻¹	21.2	Inlet m ³ h ⁻¹	21.2
Inlet molar flow rate, kmol h ⁻¹	318.4	Inlet molar flow rate, kmol h ⁻¹	275.0
T _{in} /T _{out} , °C	25.5/61.3	T, °C	80
Volume, dm ³	137	Membrane area, m ²	546
χ, %	41.0	θ, %	79.4
		Duty, MW	0.5
Outlet comp, mol fr.		Outlet comp, mol fr. (retentate/permeate)	
Ethanol	0.41	Ethanol	0.48/0.06
Butanal	0.23	Butanal	0.28/0.00
Acetal	0.16	Acetal	0.19/0.00
Water	0.20	Water	0.05/0.94

with the price of a module without membranes of a basic shell and tube heat exchanger derived from the Dutch Association of Cost Engineers⁴⁴.

Previous process calculations allowed the calculation of different material and energy balances involved in each process and therefore, the operating cost could be estimated. The only operating costs that will be compared are the utility costs, these being cooling water, refrigerant fluid and steam for heating. For the 'membranes case', membrane replacement every 3 years has been taken into account as well. Good functioning during this period of time has been proven for HybSi membranes at lab scale at the much higher temperature of 150 °C.³⁰ This period of time can vary depending on the membranes used. However, it is expected that in all the cases this period will increase for new generations of membranes and therefore, the influence of the membrane replacement costs will decrease in the overall process costs. The raw material costs, for ethanol and butanal, have been taken to be the same for all three cases, as the feed flow rates and

Table 9. Utility and raw material prices

Cooling water ^a	0.64 € t ⁻¹
Low pressure steam (50 psig – 147.5 °C) ¹	30 € t ⁻¹
Electric power ^a	0.038 € (kW h) ⁻¹
Ethanol 99% ^b	0.50 € L ⁻¹
Butanal 99%	0.75 € L ⁻¹

^a Supplied by PETRONOR (GROUP REPSOL), June 2010

^b Supplied by RYTTSA

conditions are identical. The costs of the reactants are anticipated to be significant and were also estimated. Other operating costs, like maintenance, overhead, sales, etc., are assumed to be the same for each case and were not included in the economic evaluation.

The utility prices were provided by PETRONOR (Group REPSOL YPF) and the price of ethanol was given by RYTTSA/REPSOL. For butanal, no large-scale producer was found, and a commercial cost price was calculated based on the high-purity lab-scale ethanol–butanal price ratio. Depending on the commercial brand this ratio varies from 1 to 1.8, and here a ratio of 1.5 was used. The cost prices for utility and raw material are given in Table 9.

For permeate condensation in the 'membranes case', a cooling system is used which requires an external refrigeration cycle to provide cooling media with a temperature of –3.5 °C. This cycle uses electricity and for easiness of calculation a Coefficient of Performance (COP) of 4 is used.⁴³ Table 10 shows that there is a large difference in utility costs, and thus the energy consumption between the three options. Relative to the base case, reactive distillation has utility costs that has increased by a factor of 2.5. The pervaporation case has a much lower energy consumption leading to a ~40% energy cost reduction. However, the processing costs are low compared with the costs of the raw materials. Membrane replacement accounts for less than 10% of the processing costs.

The energy costs of the pervaporation case are the lowest, but the capital investment is the highest at almost double that of the base case (Table 11). The pervaporation unit dominates, with ~75% of the total investment costs. The costs of the membranes are estimated to be ~0.6M€. The investment could be drastically reduced if the pervaporation process could be performed at a higher temperature as the required surface area would be much reduced. However, it is known that the acetal under investigation here is not stable at these temperatures when its concentration is above 80% (mol).²⁷ A cheaper membrane system is required to reduce the investment costs. Recalculating the total cost of producing 1 L of acetal it is found that the reactive distillation is ~10% more expensive than the base case. The main reason for this is, contrary to our expectation, the high energy consumption, and relatively high capital investment. The pervaporation and the base cases are almost identical in costs. The pervaporation case has lower energy costs but a higher investment. Considering that the energy price is continuously increasing, and the potential to reduce the membrane costs, one can conclude that the pervaporation process is, economically, the most viable in the long run.

Table 11 shows that the utility costs do not represent a high cost in terms of € L⁻¹ but the utilization of the pervaporation case leads to a reduction of 40% in these costs. The major component of the acetal price is the costs of the raw materials, and not that of the technology and utilities. Thus, for this specific specialty chemical the savings could be lower than the uncertainty in pricing of the raw materials. However, any fluctuation in the raw material

Table 10. Operating costs of each process

Process case	Utility cost (M€ y ⁻¹)			Total	Raw materials cost (M€ y ⁻¹)			Total (M€ y ⁻¹)
	Cooling	Heating	MR		Ethanol	Butanal	Total	
Conventional case	1.08	2.70	0	3.78	20.2	23.4	43.6	47.38
Reactive distillation case	2.61	5.89	0	8.50	20.2	23.4	43.6	52.10
Pervaporation case	0.66	1.68	0.19	2.53	20.2	23.4	43.6	46.13

MR – Membrane replacement

Table 11. Consumption and costs for each process

Process	Conventional	Reactive distillation	Pervaporation membrane
Steam at 3.5 bar, kg _{steam} /kg _{acetal}	1.80	3.76	1.12
Cooling water, kg _{H2O} /kg _{acetal}	33.68	78.20	19.51
Electricity, kW-h/kg _{acetal}	0	0	0.09
Total capital investment, M€	2.01	2.85	3.76
Total utility costs, M€ y ⁻¹	3.78	8.50	2.53
Total utility costs, € L⁻¹	0.07	0.14	0.04
Total raw material cost, € L ⁻¹	0.72	0.72	0.72
Total production costs, € L ⁻¹	0.79	0.86	0.76

price is the same for all three processes. The acetal prices, purely based on the raw material cost, is already 0.72 € L⁻¹ and thus, this is the lowest limit of any price for 1,1-diethoxy butane (acetal). Therefore, the lowest acetal price would be achieved with the pervaporation case (0.76 € L⁻¹). This price is slightly higher than the current diesel prices, which are about 0.7 € L⁻¹ at a petrol station (www.energy.eu/#fueltaxes 2011).

The proposed membrane based process could also be applied in some other similar processes like esterification or etherification reactions with other raw materials. Water is also a by-product in these reactions and efficient removal of it would facilitate the downstream distillation based separation processes since water forms azeotropes with many organics.

CONCLUSIONS

A model was developed and implemented in Aspen to describe the continuous production of 1,1-diethoxy butane and removal of the byproduct via a dehydration membrane and/or distillation. Three new processes where reaction and pervaporation are uncoupled were developed and evaluated in order to produce 1,1-diethoxy butane. The process in which a tubular reactor followed by a pervaporation module and a distillation column gave the most promising results. A low energy consumption of only ~60% of the base case, was combined with high conversion and reduced equipment sizing. Still the capital investment requires a significant reduction to convince a potential acetal producer. The high process conversions (~100%) were achieved because of efficient water separation in a pervaporation unit that leads to easy separation in the following distillation unit and further recycling to the reactor of only un-reacted compounds. This last process was compared with a conventional process and a reactive distillation process. The developed process in which dehydration membranes were used seems to be the most promising option because of a lower energy requirement that almost approaches the lowest possible limit. However, the utility costs do not represent a high cost in

terms of € L⁻¹ but the utilization of the pervaporation case leads to a reduction of ~40% in these costs. The major component of the acetal price is the costs of the raw materials, and not that of the technology and utilities. This process concept would also be applicable in other similar processes based on esterification or etherification reactions. From the process point of view, efficient water removal avoids the formation of azeotropes in the downstream distillation columns facilitating the separation and reducing the column height from 51 to 16 m. Moreover, advances in pervaporation membrane technology and modules fabrication, trying to lower the investments required in combination with increasing energy prices, will favor even a higher difference between this alternative and the other processes. Besides, some smart membrane module configurations like using a multi-step system with different permeate pressures would lead to a decrease in the price of the cooling system, as the first modules would not require really low permeate pressures.

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