

Case Study : An Energy efficient way to retrieve Ethyl acetate from a waste stream

1 Introduction

PERVATECH BV established in 1999 is a leading company in membrane technology. Based on the belief that we have an obligation towards future generations to preserve Earth's resources we develop products and services that enable customers to innovate their products and production processes towards lower energy consumption, less waste and higher quality. We produce membranes, membrane modules and systems for pervaporation and vapour permeation applications.

In this case study we present an energy efficient method to reduce Ethyl acetate rich waste streams and recover as much ethyl acetate as possible, thereby lowering the purchase of new clean solvent.

2 Case Study

Ethyl acetate (figure 1) is synthesized in industry by different reaction routes. The main reaction route is the Fischer esterification reaction of ethanol and acetic acid in which ethyl acetate and water is being formed. The reaction formula of this esterification, which is often catalysed by sulphuric acid, is depicted below.

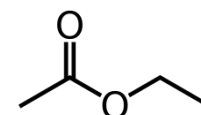
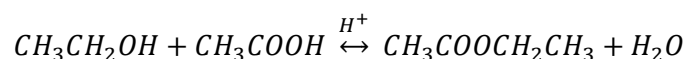
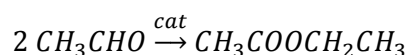


Figure 1: Ethyl Acetate

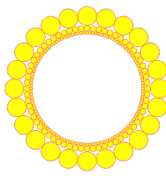


Without the removal of water, the conversion of the reaction mixture is approximately 0.65 at room temperature. This equilibrium can be shifted to the ethyl acetate side of the equation by removing water from the reaction mixture. A possible method for the removal of water from the mixture is pervaporation with hydrophilic ceramic membranes. Another synthesis route is the Tishchenko reaction which combines two acetaldehyde molecules to ethyl acetate at temperatures between 0 and 5 °C. For this reaction an alkoxide catalyst is being used like aluminium alcoholate. The Tishchenko reaction is stated below.



Ethyl acetate is mainly used as a diluent and solvent because of its low toxicity, odour and costs. Ethyl acetate is being used for the decaffeination of tea leaves and coffee beans and for the cleaning of circuit boards. Next to industrial applications ethyl acetate is also being used in cosmetics such as perfumes and nail polish cleaner. Ethyl acetate is also found in wine and contributes to the perception of fruitiness.

Since ethyl acetate forms an azeotrope with water, $x_{mole,ethyl\ acetate}=0.69$ ($x_{mass,ethyl\ acetate}=0.92$), separation of ethyl acetate and water by means of distillation is not possible in one distillation column. In order to break the azeotrope, pervaporation membranes can be used for the selective separation of water and ethyl acetate. For the dehydration three different cases have been



calculated. The first calculation is based on a pervaporation only system. The second calculation is based on a distillation up to the azeotropic point after which a membrane system takes over and dehydrates further up to spec. The third calculation is based on 2 distillation columns combined with a small membrane module for breaking the azeotrope.

3 Energy and mass balances

In order to calculate the possible energy savings for a hybrid or membrane only system, mass and energy balances were made. In this section the three cases are shown in the following order:

1. Membrane only system
2. Distillation combined with pervaporation after the from the azeotropic point up to spec.
3. Distillation combined with pervaporation for the breaking of the azeotrope.

All cases are built around the boundary conditions stated in table 1:

Table 1: Boundary conditions for case study

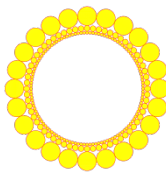
Quantity	Value	Unit
Φm_{feed}	10000	[kg/day]
$t_{\text{system uptime}}$	8000	[hour/year]
$X_{\text{mass_H2O_feed}}$	0.2	[-]
$X_{\text{mass_H2O_product}}$	0.001	[-]
$X_{\text{mass_H2O_waste}}$	0.999	[-]

3.1 Dehydration of ethyl acetate by means of pervaporation

The first mass balance is calculated for a pervaporation only system, which is in terms of energy the most economic option. The drawback of a pervaporation only system is the high membrane surface area compared to the other cases which include a distillation column for the bulk dehydration. The necessary membrane surface area for the pervaporation system is 34m^2 at $T=130^\circ\text{C}$. The Mass and energy balance for the pervaporation system is depicted in table 2. The mass balance is calculated for a feed stream of 10,000 kg/day and a running time of 8000 hours/year. The water mass fraction in the feed stream is 0.2 ($x_{\text{mole,H2O}}=0.55$) and the final water mass fraction in the end product (Retentate stream, ethyl acetate) is 0.001 ($x_{\text{mole,H2O}}=0.003$). The permeate stream still has an average ethyl acetate mass fraction of 0.17 since the selectivity for water is not infinite and therefore some ethyl acetate will permeate through the membrane at low water concentrations.

Table 2: Mass and energy balance pervaporation system

Stream	Φm [kg/h]	x_{Water} [-] weight	Q kW	Heating or cooling
Feed 1	456.3	0.200	88.3	Heating
Permeate 2	109.7	0.830	73.3	Cooling
Retentate 3	346.6	0.001	17.3	Cooling
			178.8	Total



3.2 Dehydration of ethyl acetate by means of distillation and pervaporation

The second case is a combined distillation up to the azeotropic point ($x_{\text{mass,H}_2\text{O}}=0.08$) and a pervaporation system to break the azeotrope and dehydrate the ethyl acetate up till specifications. The mass and energy balance for this case is depicted in table 3. The energy consumption of the hybrid system is slightly more than for a pervaporation only system since a distillation has to feed the top and bottom product partially back to the column in order to have an efficient separation. Due to this reflux, a distillation column is evaporating the feed more than once which is in terms of energy quite inefficient. The vapour liquid equilibrium diagram including the different stages necessary for the distillation is depicted in figure 2. On the x-axis, the mole fraction of ethyl acetate in the liquid phase is depicted. The y-axis depicts the mole fraction of ethyl acetate in the vapour phase. The necessary membrane surface area is approximately 31m^2 at $T=130^\circ\text{C}$ for the dehydration from $x_{\text{mass,water}}=0.1$ till $x_{\text{mass,water}}=0.001$. The membrane surface area is still high since the most membrane surface area demanding step, the dehydration to low water concentrations, is being performed by membranes. The dehydration from a high water concentration by means of pervaporation is relatively fast and therefore less membrane surface area demanding. The loss of organics to the permeate is covered by feeding the permeate back to the distillation column, therefore almost no ethyl acetate is lost as waste with the water stream and the ethyl acetate present in the permeation is fed to the membranes again after it passed through the distillation column. A schematic sketch of the hybrid dehydration system with one distillation column and a pervaporation system is depicted in appendix 1.

Table 3: Mass and energy balance hybrid system 1

Stream	Φm [kg/h]	x_{Water} [-] weight	Q kW	Heating or cooling
Feed	1	456.3	0.200	
Top	2	651.0	0.100	99.9
Reflux top	3	217.0	0.100	
To				
membrane	4	434.0	0.100	
Bottom	5	136.7	0.999	
Reflux				
Bottom	6	45.6	0.999	28.5
Water	7	91.1	0.999	
To				
membrane	8	434.0	0.100	29.7
To				
membrane	9	434.0	0.100	
Permeate	10	68.9	0.627	29.7
Permeate	11	68.9	0.627	
Retentate	12	365.1	0.001	18.2
			206.0	Total

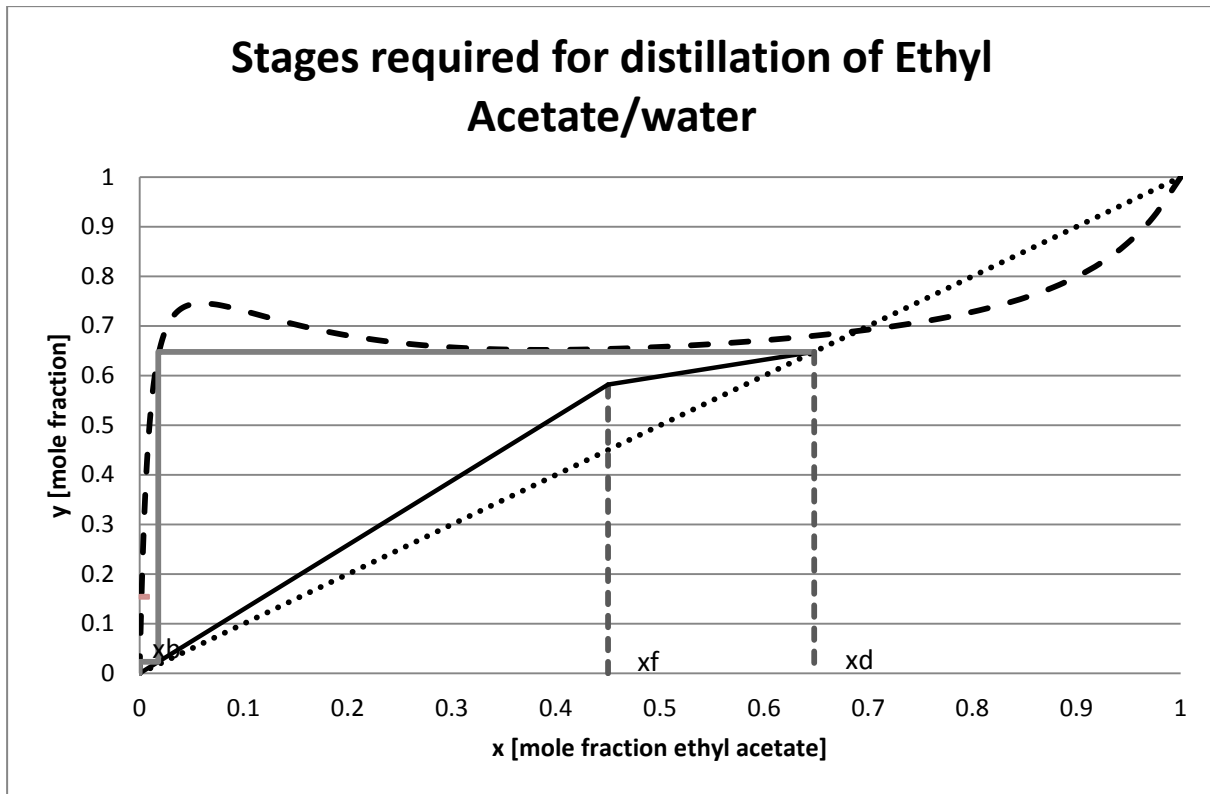
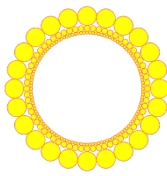


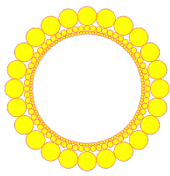
Figure 2: VLE diagram for the distillation of ethyl acetate to the azeotropic point

3.3 Dehydration of ethyl acetate by means of distillation and pervaporation for breaking the azeotrope

Since the membrane surface area required for the dehydration of ethyl acetate from the azeotropic point is still quite large, a third case was worked out for a hybrid system consisting of 2 distillation columns and a pervaporation system. A schematic sketch of this system is depicted in appendix 2. The first distillation column is being used for the water/ethyl acetate separation up to the azeotropic point while the second distillation column is separating the ethyl acetate/water mixture, after the azeotrope is being broken by the pervaporation system, up to specifications. The vapour liquid equilibrium diagram for the second distillation column is depicted in figure 3 whilst the VLE diagram for the first distillation step is depicted in figure 2. In figure 3 the x-axis depicts the mole fraction of water in the liquid phase. The y-axis depicts the mole fraction of water in the vapour phase. The mass and energy balance for this case is depicted in table 4.

Table 4: Mass and energy balance hybrid system 2

Stream		Φ_m [kg/h]	x_{Water} [-] weight	Q kW	Heating or cooling
Feed	1	456.3	0.200		
Top	2	680.3	0.100	104.4	Cooling
Reflux top	3	226.8	0.100		
To membrane	4	453.5	0.100		
Bottom	5	136.7	0.999		
Reflux Bottom	6	45.6	0.999	28.5	Heating
Water	7	91.1	0.999		
To membrane	8	1007.0	0.100	33.8	Heating



To membrane	9	1007.0	0.100		
Permeate	10	55.8	0.959	33.8	Cooling
Permeate	11	55.8	0.959		
Retentate	12	951.2	0.050		
Bottom 2	13	730.3	0.001		
Reflux Bottom 2	14	365.1	0.001	36.9	Heating
Ethyl acetate	15	365.1	0.001		
Top 2	16	1172.1	0.080	167.6	Cooling
Reflux top 2	17	586.0	0.080		
Top 2 to membrane	18	586.0	0.080		
				405.0	Total

The membrane surface area for the breaking of the azeotrope is only 3m^2 since the dehydration at higher water concentration is much faster than at low water concentration due to the higher driving force over the membrane and therefore a higher water flux. Although the membrane surface area is reduced considerably, the energy demand for this system is almost twice as much as for the pervaporation only system. Therefore CAPEX and OPEX calculations have to be performed to be able to decide which case is the best option.

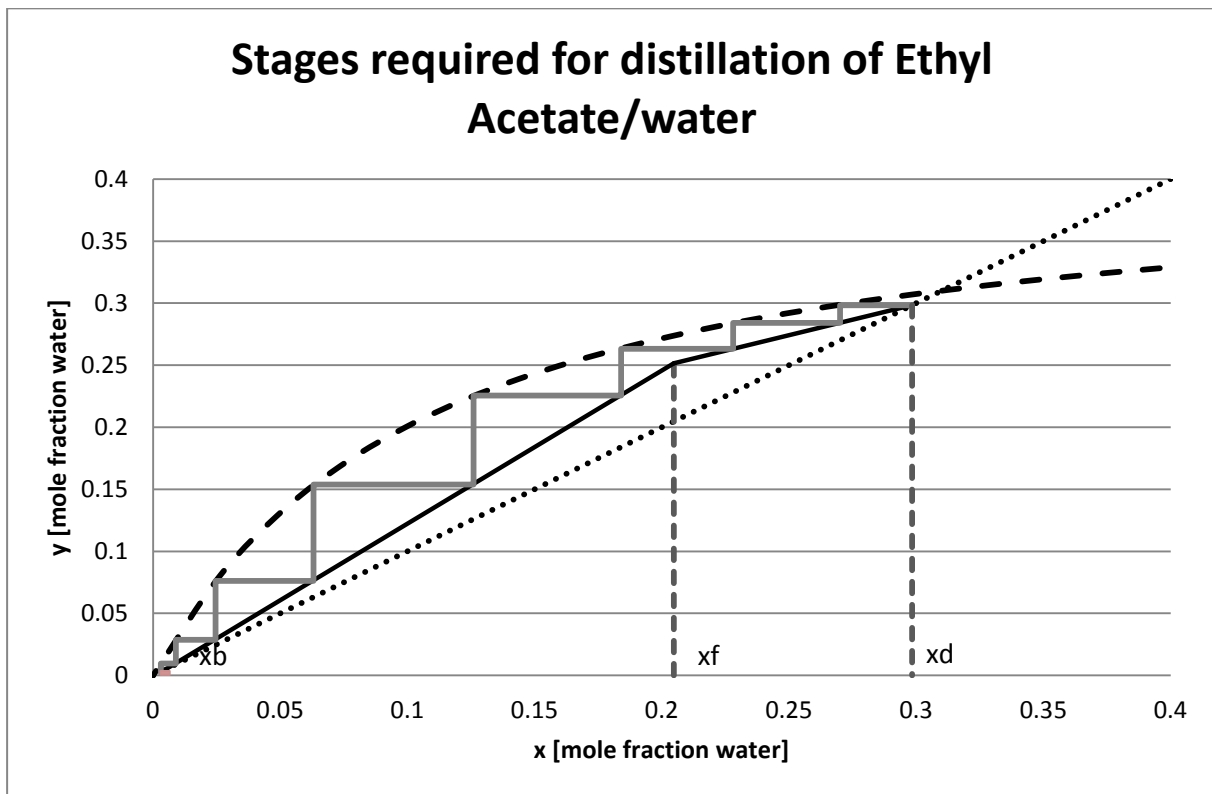


Figure 3: VLE diagram for the distillation of ethyl acetate from the azeotropic point

3.4 Energy consumption of the systems calculated in the different cases

In order to give an estimation for the operational expenditure (OPEX), the energy costs have been calculated for an ideal situation. For this calculation an energy price of 0.08 €/kWh has been used. The results of this cost estimation are depicted in table 5.

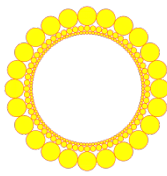


Table 5: Energy costs for the different systems

System	Q/ton product [kWh]	Q/year [MWh]	Costs for heating and cooling/year [k€]
1 Membrane only	516	1883	151
2 1 column + membrane	564	2059	165
3 2 column + membrane	1109	4049	324

Next to the estimation of the costs of heating the system, the three cases have been evaluated based on the CAPEX and OPEX for different depreciation periods and a membrane life of 3 years. The graph for the present worth (PW) and annual worth (AW) are depicted in figure 4 and figure 5. Please note that all values are normalized for publication purposes.

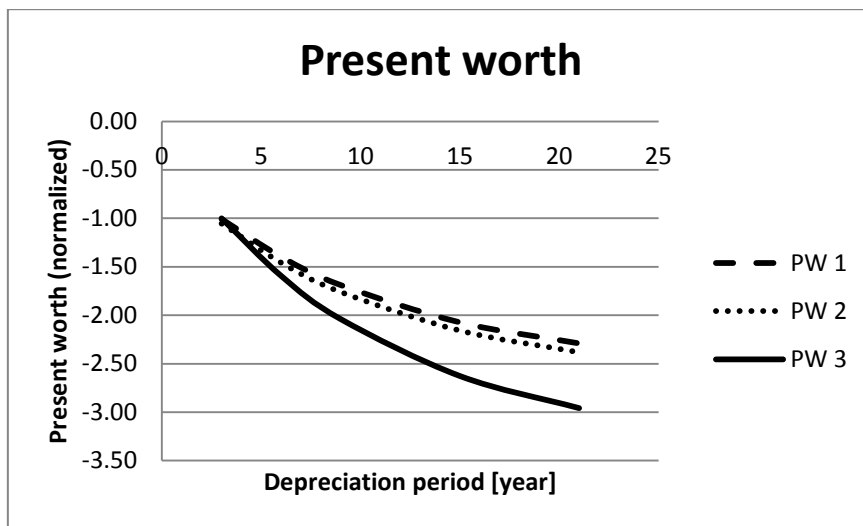


Figure 4: Present worth of a dehydration installation for different depreciation periods

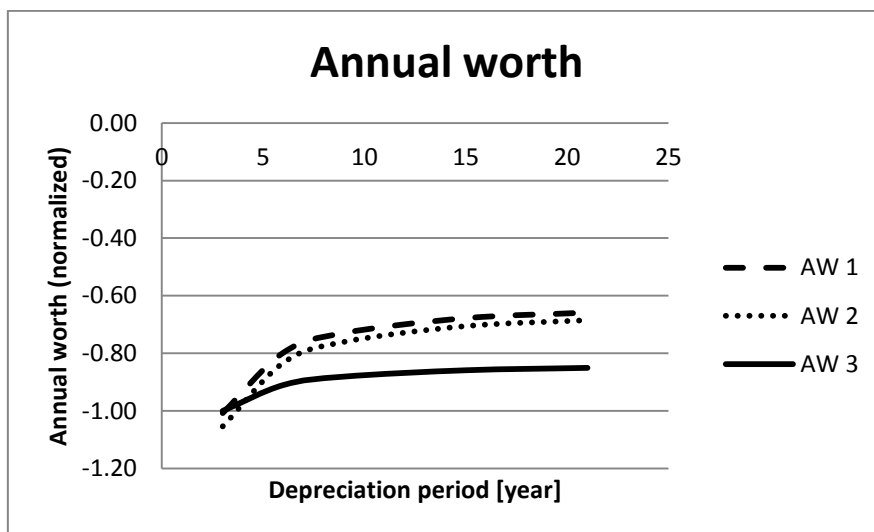
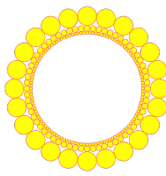


Figure 5: Annual worth of a dehydration installation for different depreciation periods



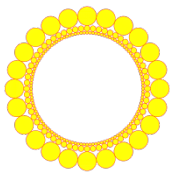
4 Conclusion

The separation of water/ethyl acetate mixtures can be simplified by applying pervaporation membranes as a standalone unit or in combination with distillation.

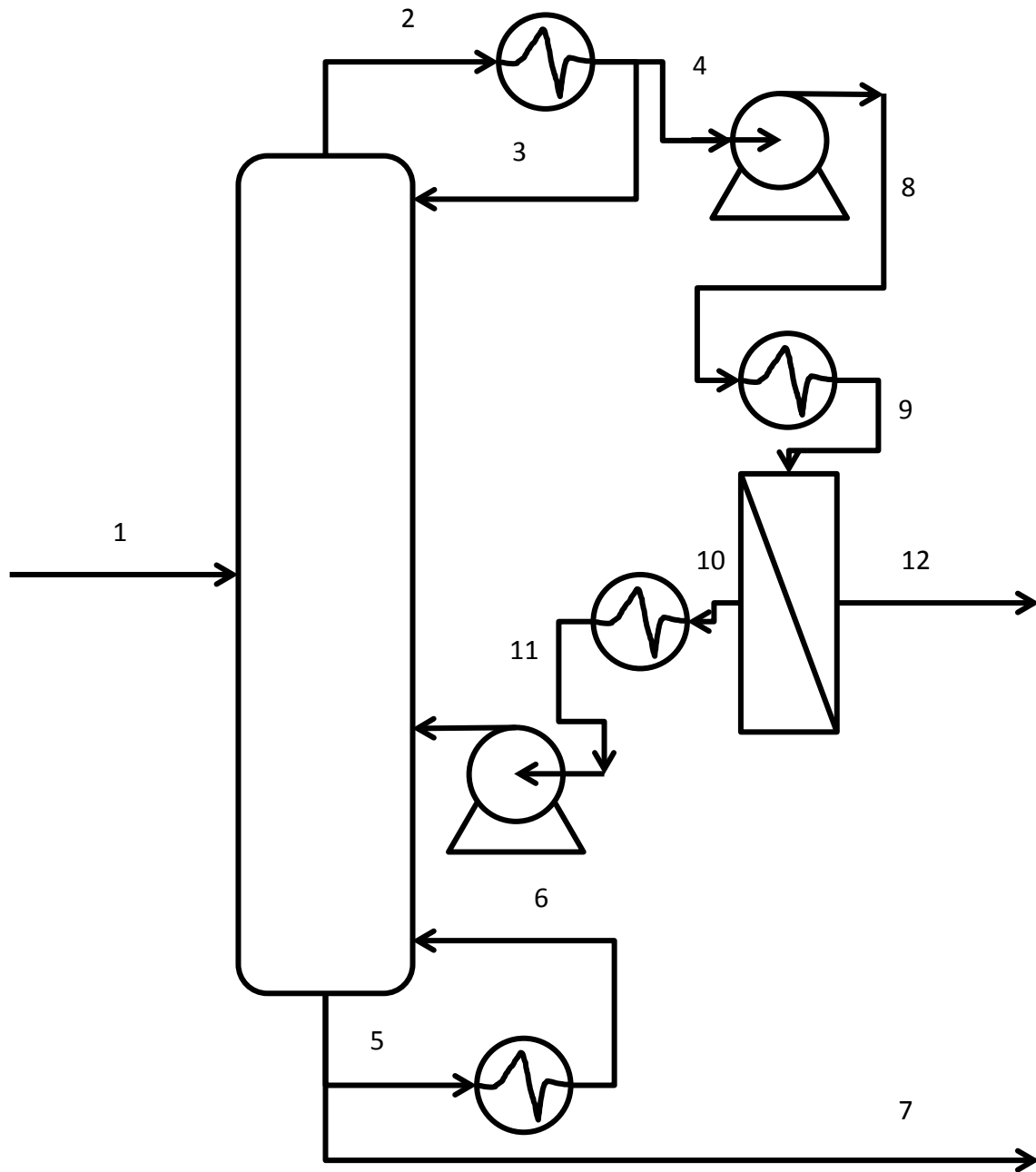
The full dehydration with membranes only has the lowest energy demand but leaves a water rich waste stream with about 17 wt.% ethyl acetate on the permeate side. This waste stream requires extra treatment or incineration.

Although the system with one distillation column combined with a pervaporation system still requires a relatively large membrane surface area, the loss of organics to the water phase is limited since it can be fed back to the distillation column to recover the ethyl acetate from the water fraction. With only a slight increase in energy consumption this might be the most economical option.

The system with two distillation columns in which the membranes are being used for the breaking of the azeotrope is quite energy demanding compared to the other systems stated in this case study. The membrane surface area is limited, therefore the CAPEX might be lower than for the other cases but the OPEX will be higher. This also follows from the annual worth calculations performed on the different cases indicating in the end lower costs for the systems in which most of the work is being done by membranes. The main driver for this outcome is the lower energy costs which can be quite substantial over time.



Appendix 1: Schematic overview of a hybrid dehydration system



Appendix 2: Schematic overview of a hybrid dehydration system 2

