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# Vapour permeation for ethanol recovery from fermentation off-gas

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## **Abstract**

In ethanol fermentations, about 2% of the ethanol leaves the fermenter with the off-gas. Conventionally, this is recovered by absorption in water. As alternative, vapour permeation was investigated conceptually for ethanol recovery from fermentation off-gas. A preliminary techno-economic evaluation of this system using hydrophobic membrane was carried out. The results were compared with conventional absorption. For the assumed membrane, concentrated ethanol (~ 66 mass%) might be achieved using vapour permeation whereas absorption achieves 2 mass%, and needs much more distillation to achieve ~ 93 mass%.

The ethanol recovery costs for base case absorption and for hydrophobic vapour permeation were calculated to be 0.211 and 1.389 US \$/kg, respectively. The ethanol recovery cost decreases with increase in membrane permeability in hydrophobic vapour permeation but the base case cost was not achieved. In the vapour permeation process, membrane cost dominates at lower membrane permeabilities whereas at the permeabilities 3 times higher than original, the costs for vacuum on permeate side of membrane governs the ethanol recovery cost.

*Keywords:* Bioprocess integration, fermentation, ethanol recovery, absorption, vapour permeation, economic evaluation.

## 1. Introduction

Bioethanol is potentially more sustainable than fossil fuels and is currently used as a fuel or fuel additive. This application leads to increasing demand for bioethanol. To compete with the fossil fuels, the bioethanol production should be cost effective. This can be achieved by increasing the process yield and productivity, and by using cheaper feedstock. Moreover, the process will require efficient and effective separation technologies [1].

Distillation is the most applied industrial process for bioethanol separation. But for dilute ethanol feed streams (ethanol concentration < 5 wt.%), distillation is relatively energy intensive [2]. For ethanol recovery from such a dilute stream, pervaporation, a membrane separation process, is one of the options that could be more economical than distillation [3, 4]. Pervaporation has additional advantages over distillation and has been investigated by many researchers [3-5].

During an integrated experiment with of two-stage fermentation coupled with pervaporation, we observed severe fouling of the pervaporation membrane [6]. The potential fouling candidates, present in the fermentation broth, have been identified and their effects on the membrane performance have been evaluated [7-9]. To regain the membrane properties fouled membrane was washed with 70% (v/v) ethanol and isopropanol. However, complete regeneration of the membrane was not attained.

One of the approaches to deal with fouling is to opt for another membrane process such as vapour permeation (VP). Here, the feed is vapour and not liquid (as in pervaporation). The separation is achieved by degrees to which components are dissolved and diffuse through the membrane [10]. Vapour-gas permeation is used industrially for recovering high value solvents, liquefied petroleum gas, for methane enrichment (removing CO<sub>2</sub>), air purification and also for removal of volatile organic compounds [11-13]. Vapour permeation is also widely studied and commercially applied for dehydration (water removal) from organic

solvent vapours such as ethanol using hydrophilic membranes [10]. The commercial-scale production of 99.9% ethanol from 94% ethanol has been achieved by water vapour permeation [14]. However, the current paper focuses on ethanol vapour permeation.

One might envisage a process option including stripping of the ethanol from fermentation broth by CO<sub>2</sub> or another gas, followed by vapour permeation for ethanol recovery. This process option avoids the circulation of fermentation broth through the membrane unit thereby avoiding membrane fouling and additionally utilizes the fermentation byproduct, CO<sub>2</sub>, which otherwise is mostly vented-off from the process. Ethanol stripping from fermentation broth by CO<sub>2</sub> and recovery by different separation techniques, such as adsorption, rectification and condensation, has been successfully demonstrated [15-17]. To our knowledge, this is the first report proposing the above mentioned process option. It might be applied industrially but needs more investigation due to possibility of many process configurations. Also, the availability of a membrane suitable for separation is a prerequisite.

However, before considering the combination of stripping and vapour permeation, we focus on vapour permeation to recover ethanol merely from off-gas in a conventional fermentation set-up. The bioethanol yield is increased by recovering ethanol from fermentation off-gas. Another reason for this recovery is the legal limit for ethanol emission from a bioethanol plant, which can be 40 t/year for example [18]. The ethanol recovery from fermentation off-gas is conventionally done by water absorption. In US-based bioethanol production processes, this recovered stream (absorber bottom outlet), being very dilute in ethanol, is recycled to an up-stream process unit such as slurry mix tank for use in corn hydrolysis [19]. The ethanol present in this stream later enters the fermentation but does not disturb it. In the Brazilian ethanol production process (Fig. 1), no water recycle is needed as cane juice, rich in water, is used as feedstock. Also, the Brazilian process uses yeast recycling and is sensitive to volatile inhibitors that are recovered together with ethanol upon absorption.

Thus, the dilute ethanol stream from the absorber is combined with the much larger and more concentrated ethanol stream originating from fermentation, and fed to the beer column [20]. The mixing of outlet streams of absorption and fermentation conceals that relatively much energy is required for recovering ethanol from the vapour stream. Vapour permeation might be used instead of absorption, for ethanol recovery from off-gas.

Thus the focus of this study is to investigate the feasibility of vapour permeation for ethanol recovery from fermentation off-gas. Vapour permeation using hydrophobic membrane will be evaluated. A techno-economic evaluation of the proposed system will be carried out and will be compared to absorption. The comparison between the conventional and proposed process will mainly be based on the ethanol concentration in the outlet of the recovery units (absorption/vapour permeation), on its effect on distillation energy consumption, and the on overall process economics.

## **2. Process description: Base case and vapour permeation case**

### ***2.1 Base case***

The conventional corn dry-grind ethanol process described in literature was considered as the base case. In this process, the ethanol from fermentation off-gas was recovered by absorption and the dilute ethanol stream was recycled back. The process shown in Fig. 1, is modification of a published case [19].

#### **<Fig. 1>**

The modification is that the absorbed ethanol is sent downstream instead of upstream, to simplify comparison of this base case with the vapour permeation case. Thus, the recovery of the ethanol from fermentation off-gas was carried out by ethanol absorption in water. The recovered ethanol (bottom outlet) was mixed with the fermentation broth stream and then fed

to the distillation. The washed CO<sub>2</sub> from the top of the absorber was vented to the atmosphere. The key data considered are given in Table 1.

**<Table 1>**

## ***2.2 Vapour permeation case***

The proposed vapour permeation process is shown in Fig. 2.

**<Fig. 2>**

Using a centrifugal compressor, the fermentation off-gas was compressed from 0.1 MPa to 0.15 MPa pressure, which was taken as reasonable value. Then, it was fed to the vapour permeation unit. A hollow fibre membrane module, consisting of hydrophobic PIM-1 membrane [21, 22], was assumed for vapour permeation. The permeate pressure was assumed to be maintained at 0.002 MPa by using a roots vacuum pump. The permeate was then liquefied in a condenser using chilled water as a coolant. The condensed stream, rich in ethanol, was fed to the distillation or directly to the ethanol dehydration unit, depending on the ethanol composition of the stream. The retentate stream, largely containing CO<sub>2</sub> and traces of ethanol, satisfying the legal ethanol emission limit, was vented to the atmosphere, similar to the base case.

Thus, in both cases, the fermentation is identical and does not need to be designed. Also, the ethanol dehydration does not need to be designed, assuming that in both cases all ethanol vapour from the off-gas is converted to 93 mass% ethanol, suitable for dehydration.

### 3. Design Methods:

#### 3.1 Base case

The mass balances for the absorption were derived from the simulation of the base case process in SuperPro Designer<sup>®</sup> software (Intelligen Inc., Scotch Plains, NJ) [19]. The results thus obtained were further used for economic evaluation.

#### 3.2 Vapour permeation case

##### 3.2.1 Compressor

An adiabatic centrifugal compressor was assumed in the proposed configuration. It was assumed that the stream flow rate and its composition remain the same upon compression. The stream outlet temperature ( $T_2$ ) to compress the off-gas from the inlet temperature ( $T_1$ ) of 303.15 K and the feed pressure ( $p_1$ ) of 0.1 MPa to the outlet pressure ( $p_2$ ) of 0.15 MPa was calculated using standard equation for adiabatic compression. The constant  $K$  in this equation is the ratio of specific heat capacity at constant pressure ( $C_p$ ) to specific heat capacity at constant volume ( $C_v$ ) [23]. These specific heat capacities were taken for CO<sub>2</sub> at standard conditions since this is the major component of the off-gas.

The energy needed for the required compression was calculated using the standard equation which gives the adiabatic heat ( $H_{AD}$ ) [23]. The compressibility factor ( $C^f$ ) in this equation was assumed to be 0.99.

The total power required for compression ( $P_{comp}$ ) was calculated using Eq. (1).  $F_{comp}$  is compressor feed flow rate and  $\eta_{comp}$  is mechanical efficiency of the compressor. The compressor efficiency was assumed to be 75%.

$$P_{comp} = \frac{F_{comp} \cdot H_{AD}}{\eta_{comp}} \quad (1)$$



### 3.2.2 Vapour permeation

Permeate and retentate flows and compositions, flux through the membrane, and membrane area required for ethanol recovery were determined by solving the mass balance equations across the membrane as indicated below.

The summation of mole or mass fraction of components on permeate side ( $Y_i$ ) and retentate side ( $Z_i$ ) is given by,

$$\sum Y_i = 1; \quad \sum Z_i = 1 \quad (2)$$

The feed and permeate side component balances for the vapour permeation unit are denoted by Eq. (3) and (4),

$$F_m \cdot X_i = R_m \cdot Z_i + J_i \cdot A_m \quad (3)$$

$$J_i \cdot A_m = Y_i \cdot P_m \quad (4)$$

where  $F_m$ ,  $R_m$  and  $P_m$  are membrane feed, retentate and permeate molar or mass flows.  $X_i$  is mole or mass fraction of component  $i$  in the feed with  $i = \text{CO}_2$ , ethanol or water.  $A_m$  is the membrane area required for the separation and  $J_i$  is the component molar or mass flux through the membrane and was calculated using Eq. (5) [24],

$$J_i = \frac{P_i^e}{l} (p^F \cdot X_i - p^P \cdot Y_i) \quad (5)$$

$P_i^e$  indicates the component permeability through the membrane,  $p^F$  and  $p^P$  are pressures at feed and permeate side and  $l$  is the membrane thickness. The calculation of component mass fluxes were carried out by converting molar based membrane permeabilities to mass based using molar masses.

Plug flow model was approximated by assuming a series of mixed sections, with 20 mass% permeation of the ethanol in feed of each section i.e. 20% of the ethanol entering a stage is permeated in that stage. For simplicity, potential deviations from plug flow were

neglected [25]. The sections are no formal process stages and there are no physical barriers between stages. The retentate obtained in a previous section was then considered as feed for a next. Because  $(0.8)^{20} \approx 0.01$ , which is a reasonable fraction for ethanol not recovered, we performed calculations with 20 sections and 0.8 retention per stage.

The mass balance and flux equations, mentioned earlier, with an additional equation of

$$R \cdot Z_e = 0.8 \times (F \cdot X_e) \quad (6)$$

were solved by iteration till the legal ethanol emission limit was achieved and the membrane area needed for each section was determined. During these calculations, the pressure drop over the membrane fibre length was considered to be negligible (discussed in section 5.1).

**<Fig. 3>**

The overall permeate flow was obtained by summing the permeate flows of all sections, and the overall permeate composition was obtained by averaging according to Eq. 7 (Fig. 3). For simplicity, the reversibility term in the flux calculation was neglected for CO<sub>2</sub>.

$$\text{Average permeate composition} = Y_{i,j} = \frac{\sum_{j=1}^l P_j \cdot Y_{i,j}}{\sum_{j=1}^l P_j} \quad (7)$$

PIM-1 membrane was considered for hydrophobic vapour permeation. This membrane was selected on the basis of availability of membrane parameters. The ethanol and water permeabilities for PIM-1 membrane were determined during ethanol-water pervaporation whereas for CO<sub>2</sub> it was determined during gas permeation at 303.15 K. The ethanol and water permeabilities at higher temperature (332.15 K) were calculated using the literature data for 10 wt.% ethanol-water solution and their corresponding equilibrium vapour pressures at this temperature. The resulted PIM-1 membrane parameters were further used for mass balance calculations and are listed in Table 2 [21, 22].

**<Table 2>**

Hollow fibre membrane modules were assumed for vapour permeation. To calculate the pressure drop ( $\Delta p$ ) across the membrane fibre, the modified Hagen-Poiseuille equation incorporating gas compressibility and fibre permeability was applied [26]. The gas compressibility and fibre permeability terms were determined for the VP case in this study and were found to be negligible. This resulted in the original Hagen-Poiseuille equation (Eq. 8), as mentioned below, which was used to calculate the pressure drop.

$$\Delta p = \frac{128 \cdot \mu \cdot L \cdot F_m^v}{\pi \cdot d^4} \quad (8)$$

Here  $\mu$  is the kinematic viscosity of the gas (based on CO<sub>2</sub>),  $L$  is the length of the membrane,  $F_m^v$  is the feed volume flow rate and  $d$  is the inner membrane fibre diameter.

### 3.2.3 Condenser

A shell and tube type condenser, operating under the vacuum, with counter-current flow of vapour and coolant was assumed. The hot vapour flows through the shell side under vacuum whereas the coolant, the chilling water, flows through the condenser tubes.

The sensible heat flow removed ( $Q_{R,V}$ ) by the coolant (chilled water) in the condenser was calculated using an energy balance (Eq. 9) [23].

$$Q_{R,V} = m_i \cdot C_{P,i} \cdot (T_{out} - T_{in}) \quad (9)$$

$m_i$  is molar flow of components in the hot vapour whereas  $T_{out}$  and  $T_{in}$  are outlet and inlet temperatures of hot and cold vapour, respectively. As the coolant temperature was above the boiling point of CO<sub>2</sub> and the solubility of CO<sub>2</sub> in water-ethanol solution was considered to be negligible (<0.1%)[27], it was assumed that only ethanol and water were condensed while CO<sub>2</sub> was emitted to the atmosphere. The heat flows of condensation ( $Q_{C,i}$ ) for ethanol and water were calculated from their heat of vaporisation ( $\Delta H_{V,i}$ ) using Eq. (10).

$$Q_{C,i} = m_i \cdot \Delta H_{V,i} \quad (10)$$

The total heat flow removed ( $Q_T$ ) is the sum of sensible heat flow ( $Q_{R,V}$ ) and heat flow of condensation ( $Q_{C,i}$ ). The log mean temperature difference ( $\Delta T_{LM}$ ) and the heat transfer area required ( $A_T$ ) were determined by using standard formulae. The overall heat transfer coefficient ( $U$ ) required was assumed to be 300 W/(m<sup>2</sup> K) [28].

The parameters used during calculations are given in Table 3.

<Table 3>

### 3.2.4 Vacuum pump

The power required for the vacuum pump ( $P_{vac}$ ) to maintain the desired vacuum on the permeate side of a membrane was calculated using Eq. (11) [29].

$$P_{vac} = \frac{S_0 \cdot \Delta p}{\eta_{mech}} \quad (11)$$

Here  $S_0$  indicates pumping speed of a vacuum pump without counter pressure,  $\eta_{mech}$  is the mechanical efficiency of the vacuum pump and  $\Delta p$  is the pressure difference between outlet and inlet side of the vacuum pump.

### 3.2.5 Distillation energy calculation

The distillation energy needed to achieve 93 mass% of ethanol from 2 mass% and 66 mass% of ethanol in feed for base case and vapour permeation case respectively, was evaluated based on literature data [19, 30]. A graph of ethanol recovery energy (MJ/(kg–ethanol)) against feed ethanol concentration (mass%) was used [30]. Annual distillation energy required was then calculated based on the annual ethanol production from this recovered stream.

### 3.3 Process Economics

#### 3.3.1 Purchased Equipment Cost (PEC)

All the cost calculations were done in US dollars (\$). The equipment cost for the base case were taken from the literature [19] whereas for the vapour permeation case the equipment costs, except the membrane costs, were determined from a website [31]. As the ethanol recovered stream flow from absorption and vapour permeation was small compared to fermenter outlet flow to distillation, the distillation equipment costs mentioned in the literature cannot be directly used. The distillation equipment cost for the base case was calculated by taking the mass flow ratio of aqueous stream from the absorption to aqueous stream from the fermenter and multiplying this with the distillation equipment costs given in literature. The resulting mass flow ratio of aqueous streams for absorption was 0.167. The distillation equipment cost from literature includes the cost of a beer column and a rectification column [19]. For the vapour permeation case, the distillation equipment cost was determined by using Aspen plus simulator (Aspen Plus V8.2). A single distillation column (module: DTW Trayed DIST1) fed with permeate flow of vapour permeation, having a distillate to feed mole ratio of 0.5 and reflux ratio of 1.2, was assumed for calculations. The simulation resulted in the distillate with desired ethanol concentration (i.e. 93 mass%) and the distillation column comprising of 26 sieve trays, a height of 16 m and a diameter of 0.46 m. The equipment cost obtained from this simulation was used for cost calculations without further price correction.

The base year for equipment costs for base case and vapour permeation case were 2008 and 2014, respectively, whereas the base year for membrane cost was 2000. The adjustment of the prices from base year to 2015 was carried out using Eq. 12.

$$Cost_{2015} = Cost_{Base\ year} \cdot \left( \frac{CEPCI_{2015}}{CEPCI_{Base\ year}} \right) \quad (12)$$

CEPCI are the Chemical Engineering Plant Cost Indexes. The indexes for years 2000, 2008, 2014 and 2015 were 394.1, 575.4, 576.1 and 556.8, respectively [32].

The cost of the vapour permeation unit was based on the total membrane area needed. A membrane capital cost of 200 \$/m<sup>2</sup> (including modules) with replacement cost of 100 \$/m<sup>2</sup> and with a membrane life of 5 years was assumed without any price correction to 2015 [3]. A centrifugal compressor made of carbon steel and with maximum compression capacity of 0.8 MPa was selected for costing. A condenser with carbon steel shell under vacuum and stainless steel (SS316) fixed U-shaped tubes was chosen.

### *3.3.2 Fixed capital investment*

The fixed capital investment for the base case and vapour permeation case was estimated by using typical factors for fluid processes [23]. These factors are given in Table 4.

**<Table 4>**

### *3.3.3 Variable costs*

Variable costs constitute of raw material, utility and shipping costs. In our study, within the battery limit considered, raw material was not necessary in either case. Only utility costs, different for both cases, were considered.

### *3.3.4 Total recovery costs*

The annual recovery cost or total recovery cost was calculated based on the variable costs, fixed cost and general expenses. The factors used for this calculation are listed in Table 5.

**<Table 5>**

## 4. Results

Here the results consisting of mass and energy flows for both process options are presented.

### 4.1 Base case

The fermentation off-gas stream size; its composition and the absorber outlet stream specification are listed in Table 6.

#### <Table 6>

A calculation of off-gas composition based on vapour liquid equilibria of a pure ethanol-water mixture, showed lower ethanol content in vapour phase as compared to that in assumed fermenter off-gas (Table 6) [19]. This contradiction can be explained by the increase volatility of ethanol due to other solutes [33]. For the ease of calculations and comparison, the composition stated in Table 6 was kept.

### 4.2 Vapour permeation case

#### 4.2.1 Off-gas compression

The fermenter off-gas composition was the same as in the base case. The compression power required to increase the feed pressure from 0.1 MPa to 0.15 MPa was 134 kW. The resulting compressed stream was at 332.15 K.

#### 4.2.2 Vapour permeation

The stream compressed to 0.15 MPa and at 332.15 K was fed to the hollow fibre tubes. Permeation of the components occurs, based on their membrane properties, and the permeate was collected under vacuum (0.002 MPa pressure) at the shell side of the module (Fig. 3).

During the calculations, using membrane permeabilities given in Table 2, the legal ethanol emission limit could not be achieved. This was due to the presence of less water than ethanol in the feed, whereas membrane permeabilities of water and ethanol were almost the same. These conditions led to faster removal of water than of ethanol. To avoid this, the ethanol permeability was assumed to be twice the value given in Table 2. The results achieved for membrane area, flow rates and their compositions are given in Table 7.

The membrane area required for vapour permeation depends on the membrane properties and the multiplication factor used in Eq. 6 (0.8), which determines the extent of ethanol retention percentage. The multiplication factor in Eq. 6 was assumed in order to calculate enough theoretical stages for good plug flow behaviour.

**< Table 7 >**

#### 4.2.3 Condenser

The permeate stream from vapour permeation was condensed using chilled water. Ethanol rich condensate (66.08 mass%) was achieved as only ethanol and water were assumed to condense. The condenser specifications and the results are given in Table 8.

**<Table 8>**

#### 4.2.4 Vacuum pump

The vacuum of 0.002 MPa on the permeate side of the membrane was achieved by using a roots vacuum pump [29]. The capacity and energy requirement of the vacuum pump were determined on the basis of permeate volume flow of uncondensed gas (here CO<sub>2</sub>). Permeate mass flow was converted to volume flow using the molar density of CO<sub>2</sub> calculated at 283.15 K and 0.002 MPa and it resulted in 42,055 m<sup>3</sup>/h. The maximum pumping speed used for a vacuum pump without back pressure was 17,850 m<sup>3</sup>/h [29]. The mechanical efficiency of the pump was assumed to be 85% and the maximum power required for a



vacuum pump, calculated using Eq. 11, was 583 kW. To meet the required permeate volume flow, three vacuum pumps were considered and the results obtained for a single pump were multiplied by factor 3.

### **4.3. Process Economics**

#### *4.3.1 Purchased Equipment Cost (PEC)*

The purchased equipment costs for the process units are given in Table 9. All indicated prices of equipment contribute significantly. The equipment costs of vapour permeation and condenser are affected by the required membrane and heat transfer area, respectively.

Because no price was available for a roots vacuum pump, a large, cast iron 1–stage blower was assumed as vacuum pump for the equipment costing and the calculation was based on permeate flow of uncondensed gas (24,752 ft<sup>3</sup>/min) [31]. Two vacuum pumps of maximum flow capacity of 22,000 ft<sup>3</sup>/min were considered. The distillation equipment cost was calculated as discussed in section 3.3.1 and the results are given in Table 9. This table shows those membrane unit costs dominate.

**<Table 9>**

#### *4.3.2 Fixed capital investment*

The fixed capital investment for both the cases was calculated based on the parameters given in Table 4 (section 3.3.2). The resulting fixed costs are shown in Fig. 4.

#### *4.3.3 Variable costs*

Variable costs were calculated on annual basis as shown in Table 10. [19, 23, 34].

**<Table 10>**

In the base case, the ethanol concentration achieved in absorber outlet stream was 1.94 (mass%) whereas in the hydrophobic vapour permeation case the concentration attained was 66.08 (mass%). To compare the two processes, the ethanol concentration should be same in both cases and was assumed to be 93% (mass%). To achieve this, the recovered stream from the absorber and the permeate condensate stream from vapour permeation were sent to the distillation. The annual distillation energy, needed to achieve the required ethanol concentration, was determined as described in section 3.2.5. The total energy cost was evaluated based on the steam cost [19]. Distillation equipment cost was calculated as explained in section 3.3.1. The total energy cost required to get 93% (mass%) of ethanol was added as variable cost to the both cases (Table 10). Comparing the utility costs for both cases, distillation and vacuum pump were the most significant contributor for base case and VP case, respectively.

#### *4.3.4 Total recovery costs*

The annual recovery costs for the hydrophobic vapour permeation case was split in two parts, namely cost of the vapour permeation unit and cost of the rest. This was done because maintenance and membrane replacement for vapour permeation were calculated based on membrane area required at a rate of 100 \$/m<sup>2</sup> and was included in the fixed costs. Thus for both parts, purchased equipment costs, fixed capital investments and fixed cost were calculated separately. The results are shown in Fig. 4.

<Fig. 4>

#### *4.3.5 Ethanol recovery cost*

The ethanol recovery cost was calculated for two schemes using total annual recovery cost and annual ethanol production. The results obtained (Fig.4 and Table 11) indicate that the

membrane process is more expensive than the conventional absorption–distillation process. Membrane and vacuum costs dominate the overall costs in the membrane process. The ethanol recovery cost obtained with hydrophobic vapour permeation was almost 6 times of that achieved with the base case.

#### <Table 11>

Note that the literature reports cost of ethanol recovery from fermentation broth of 0.05–0.15 \$/kg including cell removal [35]. However, this involves distilling relatively concentrated ethanol. Recovering ethanol from off–gas will be more expensive.

On the basis of Cost Estimate Classification System guidelines developed by AACE international, the complexity of the process proposed here can be considered in Class 4. Hence the accuracy range of cost estimation in this research is between -30% and +50% [36].

## 5. Sensitivity analysis

### 5.1 Effect of better membrane properties

The effect of an increase in membrane permeability in vapour permeation on the membrane cost, compression cost, condensation cost, and ethanol recovery cost was evaluated.

The membrane permeabilities mentioned in Table 2 were multiplied by factors ranging from 10 to 50 and the calculations for membrane area and ethanol recovery cost were repeated. During these calculations, the ethanol permeability was additionally multiplied by a factor 2 as discussed in section 4.2.2. The increase in membrane permeability results in a faster separation which causes decrease in membrane area required for separation and hence reduces the membrane cost (Fig. 5). However, this is an optimistic scenario anticipating on further developments in membrane technology. The vacuum and compression cost, which

comprise of equipment cost and utility cost, remained unchanged as membrane permeability does not affect these costs.

**<Fig. 5>**

The overall effect of variation in membrane permeability can be seen on ethanol recovery cost. The ethanol recovery cost follows a similar trend as membrane cost and decreases with increasing membrane permeability. At the initial membrane permeabilities, ethanol recovery cost was affected more by membrane cost than by other costs. However, the ethanol recovery cost for base case (0.211 \$/kg) was not achieved even at 50 times higher membrane permeability than originally. This was due to the fact that, at permeabilities 3 times higher than original, the vacuum cost becomes higher than the membrane cost and hence dominates the ethanol recovery cost. This leads to a minimum in ethanol recovery cost of 0.622 \$/kg at 50 times membrane permeability, still 3 times higher than the base case cost (0.211 \$/kg).

The higher vacuum cost was due to a larger flow of uncondensed gas ( $\text{CO}_2$ ) through the vacuum pump which increases the energy requirement for maintaining the desired vacuum. The cost calculations were also performed based on ethanol–water permeate flow only, thus assuming a  $\text{CO}_2$ –impermeable membrane. The resulting ethanol recovery cost at 50 times higher permeability was 0.411 \$/kg, which is still higher than the base case cost. The vacuum calculations were checked using the data presented by Peters and Timmerhaus [37], and the results obtained were found to be in the same range of those presented here.

The role of membrane thickness as additional variable in decreasing the ethanol recovery cost was identified (Eq. 5). Instead of increasing the membrane permeability, the membrane thickness can also be reduced. This can result in higher fluxes through the membrane thereby decreasing the membrane area needed for the desired separation and hence the ethanol cost.

It was checked if a pressure drop might occur over the length of the membrane in the hollow fibre vapour permeation module. Based on required membrane area (Table 7), the number of fibres was 656,200 when using single fibre dimensions of 1.6 m × 2 mm (length × inner diameter). The pressure variation in the hollow fibre membrane module can be caused due to friction of gas molecules and by the permeation of the gas. The change in the pressure, at the outlet of the fibre, due to these factors was calculated using the modified Hagen–Poiseuille equation (see section 3.2.2; Eq. 8). It was found that the pressure loss across the membrane fibre was negligible.

### 5.2 Different membrane type – Hydrophilic membrane

A similar analysis as that for hydrophobic vapour permeation, was performed using a hydrophilic membrane, such as alginate based (separation layer: alginate, membrane support: PVDF, chitosan; total flux = 0.172 kg/(m<sup>2</sup>h) and  $\alpha_{water/ethanol} = 90$  at 323.15 K) [38]. In this case, it was assumed that dehydration of fermenter off-gas was carried out and the permeate mainly containing water and ethanol (satisfying the legal emission limit) was vented. The retentate, after condensation, will produce an ethanol rich stream with ethanol composition of 95 mass%.

During hydrophilic vapour permeation calculations, it was tried to apply the legal ethanol emission limit on the permeate side (permeate ethanol flow = 5 kg/h). The results achieved using this condition indicated that this constraint was not held and not even with unrealistic large values for the membrane area required. Therefore, this ethanol emission constraint should not be applied immediately at the permeate side of the vapour permeation because even for a very good membrane too much ethanol will permeate when most of the water needs to permeate. Besides, the ethanol lost with uncondensed CO<sub>2</sub> in the retentate should also be taken into account while applying the emission limit.

Thus, a more complex process option, such as recycling of the permeate stream to a stripping column for heat recovery, permeate stream condensation, etc. may be necessary to meet the ethanol emission limit when using a hydrophilic membrane [30, 39]. Evaluation of such process option will require a separate study and this is considered to be out of scope of the present research. Also, for plants with a different ethanol production capacity, the vapour permeation case will remain more expensive than the base case, because the base case is cheaper with respect to both capital investments and variable costs.

## **6. Conclusions**

Vapour permeation using hydrophobic membrane for ethanol recovery from fermentation off-gas was proposed and techno-economic comparison was carried out against conventional absorption process. In the vapour permeation case, the ethanol concentration obtained in the recovered stream was 66.08 mass% and was very high compared to the concentration in the absorber outlet (bottom) stream (1.94 mass%). Consequently, the mass flow rate of the dilute absorber stream was very high.

The energy cost needed to distil the absorber and condensed permeate of vapour permeation to achieve 93 mass% ethanol was added and ethanol recovery cost was calculated for both process options. The recovery cost obtained indicates that the membrane process is much more expensive than the conventional absorption–distillation process. Besides the membrane costs, vacuum costs dominate the overall costs in the membrane process.

The sensitivity analysis carried out by varying membrane properties in hydrophobic vapour permeation showed that the ethanol recovery cost decreases with increase in membrane permeability but the base case cost was not achieved. In the vapour permeation process, at membrane permeability higher than 3 times original permeability, the vacuum cost becomes larger than the membrane cost.

## Nomenclature:

$\alpha$	= Membrane selectivity
$A_m$	= Membrane area (m <sup>2</sup> )
$A_T$	= Total heat transfer area in condenser (m <sup>2</sup> )
$C^f$	= Compressibility factor
$C_P$	= Specific heat capacity at constant pressure (J/(mol K))
$C_V$	= Specific heat capacity at constant volume (J/(mol K))
$d$	= Inner membrane fibre diameter (m)
$F_{comp}$	= Compressor feed flow rate (mol/h)
$F_m$	= Feed flow rate to VP (mol/h)
$F_m^v$	= Feed volume flow (m <sup>3</sup> /s)
$H_{AD}$	= Adiabatic heat (J/mol)
$H_{v,i}$	= Heat of vaporization (J/mol)
$J_i$	= Flux of component $i$ through the membrane (mol/(m <sup>2</sup> h))
$K$	= Capacity ratio
$L$	= Membrane fibre length (m)
$l$	= Membrane thickness (m)
$m_i$	= Molar flow of component $i$ (mol/h)
$P_{comp}$	= Power required for compression (W)
$P_i^e$	= Permeability of component $i$ (mol m/(m <sup>2</sup> h Pa))
$p^F$	= Feed pressure in VP (Pa)
$P_m$	= Permeate flow in VP (mol/h)
$p^P$	= Permeate pressure in VP (Pa)
$P_{vac}$	= Power requirement for vacuum pump (W)
$Q_{C,i}$	= Heat flow of condensation (J/h)
$Q_{R,V}$	= Heat flow removed from hot vapour (J/h)
$Q_T$	= Total heat flow removed by condenser (J/h)
$R$	= Gas constant (= 8.312 J/(mol K))
$R_m$	= Retentate flow in VP (mol/h)
$S_0$	= Pumping speed of vacuum pump without counter pressure (m <sup>3</sup> /s)
$T$	= Temperature (K)
$T_{cold,in}, T_{cold,out}$	= Temperature of cold stream inlet and outlet respectively (K)
$T_{hot,in}, T_{hot,out}$	= Temperature of hot stream inlet and outlet respectively (K)
$U$	= Heat transfer coefficient (W/(m <sup>2</sup> K))
$X$	= Composition on the feed side
$Y$	= Composition on the permeate side
$Z$	= Composition on the retentate side
$\mu$	= Dynamic viscosity of gas (CO <sub>2</sub> ) (Pa s)
$\eta_{comp}$	= Mechanical efficiency of compressor (fraction)
$\eta_{mech}$	= Mechanical efficiency of vacuum pump (fraction)

*Sub-/Super-script:*

$i$	= Components (Ethanol, CO <sub>2</sub> and water)
$c$	= CO <sub>2</sub>
$e$	= Ethanol
$w$	= Water
$\Delta$	= Difference
$\Sigma$	= Sum
1	= Inlet side
2	= Outlet side

**Acknowledgement**

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**List of Tables:**

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Fermentation pressure	0.1	MPa
Ethanol mass fraction in fermenter	0.108	

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Membrane	Permeability (kg m/(m <sup>2</sup> h Pa))			Membrane thickness (m)
	Ethanol	CO <sub>2</sub>	Water	
PIM-1	1.56×10 <sup>-9</sup>	6.12×10 <sup>-11</sup>	1.69×10 <sup>-9</sup>	40×10 <sup>-6</sup>

**Table 3.** Parameters used in condenser calculations.

	Components	$C_p$ (kJ/(kg K))	$\Delta H_{V,i}$ (kJ/kg)	Temperature <sup>a</sup> (K)	
				Inlet	Outlet
Vapour	Ethanol	1.44	837.17	332.15	283.15
	CO <sub>2</sub>	0.85	--		
	H <sub>2</sub> O	2.16	2443.89		
Liquid	H <sub>2</sub> O	4.20	--	278.15	291.15

<sup>a</sup> = Inlet and outlet temperatures for hot vapour and coolant (chilled water).

**Table 4.** Typical factors for estimating fixed capital investment [23].

Item	Costs
<i>Direct plant costs (DPC)</i>	
Purchased equipment cost (PEC)	Table 9
Equipment erection/installation	40% of PEC
Piping	70% of PEC
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<i>Fixed capital investment (FCI)</i>	DPC + IPC



**Table 5.** Estimation of total recovery costs [23].

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**Table 6.** Simulation results for base case adopted from literature [19].

Parameter	Value	Unit
<i>Fermenter off-gas</i>		
Flow rate	14675	kg/h
Mass fraction		
Ethanol	2.7	%
CO <sub>2</sub>	95.84	%
Water	1.46	%
<i>Absorber specifications</i>		
Water inlet flow rate	19863	kg/h
Water temperature	286.15	K
<i>Recovered ethanol stream</i>		
Flow rate	20399	kg/h
Mass fraction		
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**Table 7.** Vapour permeation mass balance results calculated using plug flow model at feed temperature = 332.15 K.

Membrane	Area (m <sup>2</sup> )		Flow rate (kg/h)	Composition (mass%)		
				Ethanol	CO <sub>2</sub>	Water
PIM-1	7010 <sup>a</sup>	Feed	14675	2.70	95.84	1.46
		Retentate	12510	0.03	99.86	0.11
		Permeate	2165 <sup>a</sup>	18.10 <sup>b</sup>	72.61 <sup>b</sup>	9.29 <sup>b</sup>

<sup>a</sup> = the sum of values obtained for individual sections over the length of membrane fibre.

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**Table 8.** Condenser specifications and results.

Parameter	Value	Unit
Coolant flow	17117	kg/h
Condenser flow rate <sup>a</sup>		
Inlet	2165	kg/h
Outlet	593	kg/h
Heat removed from vapour	259.60	kW
Heat transfer area	50.39	m <sup>2</sup>
Condensate composition		(mass fraction) %
Ethanol	66.08	
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**Table 9.** Purchased equipment costs for base case and vapour permeation case.

Equipment	Capacity/ Specification	Base year costs (\$)	Base year	2015 cost (\$)
<i>Base case</i>				
Absorber	13.41 m <sup>3</sup>	97,000	2008	93,864
Distillation <sup>b</sup>		144,956	2008	140,270
<i>Vapour permeation</i>				
Compressor	P = 134.09 kW	89,200	2014	86,212
Membrane Unit	A <sub>m</sub> = 7010 m <sup>2</sup>	200 <sup>a</sup>	2000	1,402,000
Condenser	A <sub>T</sub> = 50.39 m <sup>2</sup>	69,800	2014	67,462
Vacuum pump	--	176,700	2014	170,780
Distillation <sup>c</sup>		--		70,400

<sup>a</sup> = per m<sup>2</sup>.

<sup>b</sup> = The cost for the base year was calculated by taking the mass flow ratio of aqueous stream from the absorption to aqueous stream from the fermenter and multiplying this with the distillation equipment costs given in literature [19]. The resulting mass flow ratio of aqueous streams was 0.167 for absorption. The distillation equipment cost from literature includes the cost of a beer column and a rectification column.

<sup>c</sup> = The distillation equipment cost is obtained from Aspen simulation (Aspen Plus V8.2) and consists of single distillation column.

**Table 10.** Utility costs for base case and vapour permeation case [19, 23, 34].

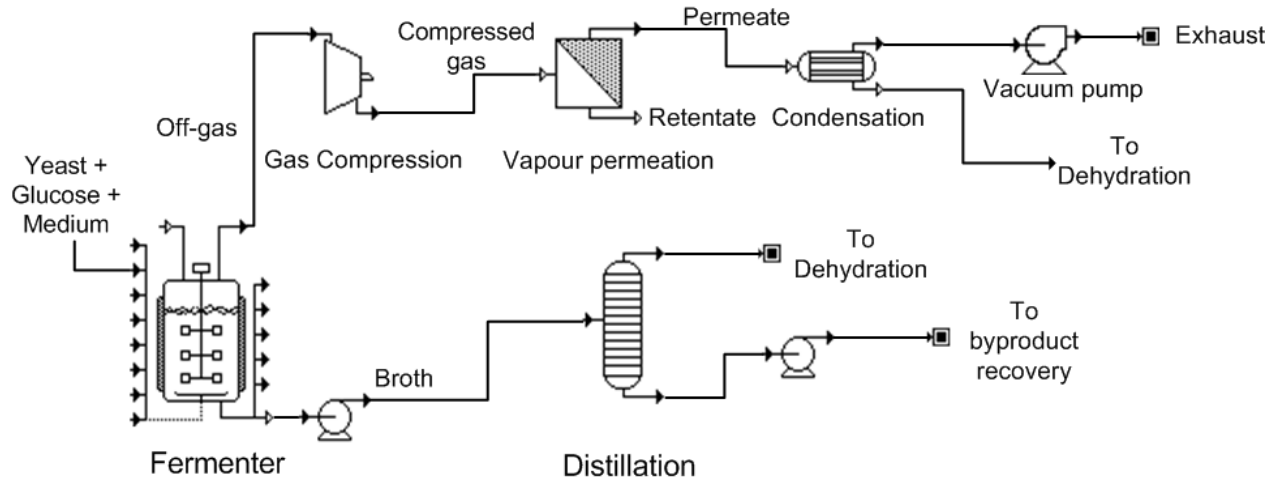
Utility	Units	Consumption	Rate	Cost (\$/year)
<i>Base case</i>				
Cooling Water	Absorber	19863 kg/h	0.07 \$/tonne	11,012
Steam	Distillation	47013912 MJ	$5.69 \times 10^{-3}$ \$/MJ	267,509
<i>Vapour permeation case</i>				
Electricity	Compressor	134.09 kW	0.0682 \$/kWh	72,428
	Vacuum pump	1749 kW		944,712
Chilled water	Condenser	17117 kg/h	0.08 \$/tonne	10,845
Steam	Distillation	9310831 MJ	$5.69 \times 10^{-3}$ \$/MJ	52,979

**Table 11.** Ethanol recovery cost for base case and vapour permeation case.

Process scheme	Feed pressure (MPa)	Membrane properties	Ethanol recovery cost (\$/kg) <sup>#</sup>
Base case	0.1	not applicable	0.211
Vapour permeation case	0.15	Permeabilities in Table 2.	1.389

<sup>#</sup> = Cf. a market price of 0.57–0.84 \$/kg fuel ethanol between April 2014 and April 2015 [40].

**Graphical abstract:**



Ethanol recovery from fermentation off-gas by vapour permeation with recovered ethanol fed to distillation.



**Highlights:**

1. Vapour permeation for ethanol recovery from fermentation off-gas was evaluated.
2. The ethanol recovery cost for hydrophobic vapour permeation was 1.39 US \$/kg.
3. The membrane process was more expensive than the conventional absorption process.
4. Dominating costs are membrane investment and replacement, and vacuum costs.

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- Fig. 1.** Base case for ethanol recovery from off-gas by conventional absorption with recovered ethanol fed to distillation (Process by [20] modified from [19]).
- Fig. 2.** Proposed process for ethanol recovery from fermentation off-gas by vapour permeation with recovered ethanol fed to distillation.
- Fig. 3.** Modeling of hollow fibre membrane module.
- Fig. 4.** Fixed costs and annual recovery costs for base case and vapour permeation case.
- Fig. 5.** Effect of increase in membrane permeability by factor  $x$  on ethanol recovery costs.

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<i>Base case</i>				
Absorber	13.41 m <sup>3</sup>	97,000	2008	93,864
Distillation <sup>b</sup>		144,956	2008	140,270
<i>Vapour permeation</i>				
Compressor	P = 134.09 kW	89,200	2014	86,212
Membrane Unit	A <sub>m</sub> = 7010 m <sup>2</sup>	200 <sup>a</sup>	2000	1,402,000
Condenser	A <sub>T</sub> = 50.39 m <sup>2</sup>	69,800	2014	67,462
Vacuum pump	--	176,700	2014	170,780
Distillation <sup>c</sup>		--		70,400

<sup>a</sup> = per m<sup>2</sup>.

<sup>b</sup> = The cost for the base year was calculated by taking the mass flow ratio of aqueous stream from the absorption to aqueous stream from the fermenter and multiplying this with the distillation equipment costs given in literature [19]. The resulting mass flow ratio of aqueous streams was 0.167 for absorption. The distillation equipment cost from literature includes the cost of a beer column and a rectification column.

<sup>c</sup> = The distillation equipment cost is obtained from Aspen simulation (Aspen Plus V8.2) and consists of single distillation column.

**Table 10.** Utility costs for base case and vapour permeation case [19, 23, 32].

Utility	Units	Consumption	Rate	Cost (\$/year)
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<i>Base case</i>				
Cooling Water	Absorber	19863 kg/h	0.07 \$/tonne	11,012
Steam	Distillation	47013912 MJ	$5.69 \times 10^{-3}$ \$/MJ	267,509
<i>Vapour permeation case</i>				
Electricity	Compressor	134.09 kW	0.0682 \$/kWh	72,428
	Vacuum pump	1749 kW		944,712
Chilled water	Condenser	17117 kg/h	0.08 \$/tonne	10,845
Steam	Distillation	9310831 MJ	$5.69 \times 10^{-3}$ \$/MJ	52,979

**Table 11.** Annual recovery costs.

Cost type	Source	Base case (\$)	Vapour permeation (VP) case (\$)		
			VP unit	Rest	Total
Purchased equipment cost	Table 9	234,135	1,402,000	396,854	1,796,854
Fixed capital investment	Table 4	882,688	5,285,540	1,488,598	6,774,138
Fixed costs	Table 5	251,566	1,943,102	424,251	2,367,352
Annual recovery cost	Table 5	662,609			4,310,395

**Table 12.** Ethanol recovery cost for base case and vapour permeation case.

Process scheme	Feed pressure (MPa)	Membrane properties	Ethanol recovery cost (\$/kg)
Base case	0.1	not applicable	0.211
Vapour permeation case	0.15	Permeabilities in Table 2.	1.389





