Direct Contact Membrane Distillation for Separation of HCl From A Mixture of Acids

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ABSTRACT

HCl is separated from HCl –H2SO4 solution by membrane distillation process(MD). The flat – sheet membranes made from polyvinylidene fluoride (PVDF) and polypropylene (pp.). Plate and frame these types of membrane where used in the process. The feed is a mixture of HCl and H2SO4 acids compositions depended on metals treated object.HCl concentration increased in the permeate during the process but sulfuric acid increased gradually in the feed .During the concentration of solution acids concentrations in the feed at the beginning were 50 g/dm³ of sulfuric acid and 50 g/dm³ of hydrochloric acid at 333K feed temperature the permeate flux was 71 dm³/m².d. At a higher concentration of HCl in the feed 111 g/dm³ and 61 g/dm³ of sulfuric acid at the feed temperature 333K volume permeate flux was 57 dm³/m².d . At a higher concentration of sulfuric acid in the feed 161 g/dm³ and 60 g/dm³ of HCl decrease the permeate flux from 71 to 35 dm³/m².d at 333K . The permeate flux increase from 35 at 333K to 85 at 343 K increase the temperature caused an increase in permeate flux. Increases in sulfuric acid concentration from 50 to 161 g/dm³ decrease the volume permeate flux from 71 to 35 dm³/m².d. HCl concentration was achieved a higher value 9.1 g/dm³ during the process at the feed concentration 161g/dm³ of sulfuric acid and 60g/dm³ of hydrochloric acid at feed temperature 343K.

Key Words: membrane distillation, HCl separation, vapor permeation
1. INTRODUCTION

Membrane distillation is a process was used for separation of two aqueous solutions with different composition and temperature, Tomaszewska and Mientka, 2009. This process takes place at atmospheric pressure and a temperature may be lower than the boiling point, Uchenna et al., 2014. A physical role of support for liquid/gas interface was played by hydrophobic membrane, and PVDF membrane prevents solution passing through it because of its nature. The driving force in membrane distillation process caused by the difference in vapor pressure across the membrane originates from the composition and temperature gradients in the boundary layer adjacent to the hydrophobic membrane, Tomaszewska et al., 2000 and Tomaszewska et al., 1998. The separation mechanism in membrane distillation process is contacted with (solution-vapor) equilibrium system, Lawson et al., 1997. When the feed contains a high concentration of volatile substance such as (HCl) with water, they all transferred from the feed side through the hydrophobic membrane pores to the distillate side, Tomaszewska et al., 1995 and Sarti et al., 1985. When the feed contains non-volatile components, so only water vapor will transferred through the membrane pores, Calabro et al., 1991. In this case the compositions of the distillate depends on the diffusion rates and volatility values for the different substances in the feed. The feed solution consisted of a mixture of sulfuric acid and hydrochloric acid with a different initial concentration, acids concentrations depends on metal treated objects, these solution is very harmful for natural environment, due to the solubility of metal oxide in sulfuric acid and hydrochloric acid, either of two acids can be used for cleaning these oxides will not be removed by the simple application or HCl only because it has a simple effect, so HCl will mix with sulfuric acid for cleaning purpose, Tomaszewska et al., 2001. Till now membrane distillation process used to concentrate of non-volatile components because MD process has been investigated widely for concentration solution of non-volatile substances. By membrane distillation process a lot of pollution problems can be solved, so the quantity of the effluents could be reduced. Membrane distillation process used for obtaining pure water from the sea, Drioli et al., 1987. Because it has been mostly investigated in salt solution of NaCl (sodium chloride), Lagnan et al., 2000. MD also has been applied to waste water treatment yielding a permeate that is less hazardous to environment the waste sulfuric acid solution can be treated by conventional methods such as (cooling, evaporation, distillation, thermal decomposition, solvent extraction), and advance method such as (membrane distillation, electro dialysis, diffusion dialysis), Petal et al., 2017. The object of this project was to recover of volatile
component from the solution and concentrate it, also to study the effect of temperature on the permeate volume flux and on the permeate concentration.

2. EXPERIMENTAL WORK

The membrane distillation process (MD), Tomaszewska, et al., 1995. Consist of feed, permeate, and two thermo-stated loops for feed and permeate to control the process temperatures. The module was plate and frame the membrane made from PVDF and supported with PP. The area of filtration was 0.045 m², membrane characteristic are pore size 0.22µm, dimensions 0.26x11.6m, H₂SO₄ rejection 99%, normal boiling point 65°C and maximum temperature 90°C for the direct contact membrane distillation, the main element of the flat sheet system was the cell consisted of compartments cold and warm, separated by hydrophobic membrane PVDF the thermo-stated feed was recycled to the warm side The vapor transported through the membrane was directly condensed in the permeate (cold side) the warm feed and cold permeate were circulated in counter current closed system as shown in Fig.1. The feed was a mixture of sulfuric acid and hydrochloric acid. The concentration of both sulfuric acid and hydrochloric acid were used in a wide range in order to investigate the effect of feed composition on the separation process. Its compositions depend on treated metal objects. The feed solutions contained HCl with initial concentration (50-111) g/dm³ whereas sulfuric acid concentration (50-161) g/dm³. The volume of feed was (3L), all experiments occurred at a feed temperature (TF in) 333 K or 343 K and the inlet temperatures of the cold receiving solution (TR in) was kept at 298 K by using thermo state loop contacting with cooler (chiller) when the permeate solution reached 298K thermo state will be turn off for all experiments, at the beginning of the process the cold system (permeate) supplied by (750ml) of distillate water to calculate the volume permeate flux, the change in the volume of distillate must be measured every hour. The concentration of Cl and H ions were measured by titration method. After each hour concentration of permeate was measured by titration method, materials were used unknown HCl solution, Phenolphthalein, NaOH solution, (2-50mL) Burette, Universal Stand, Titration Clamp,(250mL) flask, (25mL) graduated cylinder, pipet, and distilled water. Take a sample (10 ml), from permeate (HCl solution) and titration with (0.1 M) of NaOH, the base NaOH was put in the burette and acid was but in the flask, 2 drops of indicator put on the flask over the acid and titrate with base the solution was changed from colorless to pink and checked by pH meter. Volume permeate flux can be calculated by, Tomaszewska, et al., 1999.

\[ LMH = \frac{(V_{t+1} - V_t)}{A \cdot t} \, \text{dm}^3/\text{m}^2 \cdot \text{d} \]  

(1)

Where:

LMH: is the volume permeate flux

A: is membrane area, m²

\((V_{t+1} - V_t)\): are the difference in permeate volume at time \(t\) and \(t+1\)

t: the time , h
2.1 Acids

Both hydrochloric acid (HCl) and sulfuric acid (H₂SO₄) are strong mineral (inorganic) acids. They react with bases producing water and they react with metals producing H₂. HCl is found in Human body HCl drenches the stomach contents in an acid bath which kills harmful bacteria in the food. Sulfuric acid can be preparation out of the home.

2.1.1 Hydrochloric acid HCl

HCl is a solution of hydrogen chloride (HCl) gas that is dissolved in water, in the past the people called it (muriatic acid), it is widely used in industry.

Table 1. The specifications of HCl.

| Property                | Value                        |
|-------------------------|------------------------------|
| Molar density           | 36.46 g mol⁻¹                |
| Appearance              | colorless                    |
| Density                 | 1.18 g/cm³                   |
| Melting point           | -114.22 °C (-173.60 °F, 158.93 K) |
| Solubility in water     | 823 g/l (0 °C), 720 g/l (20 °C), 561 g/l (60 °C) |
| Boiling point           | -85.05 °C (-121.09 °F, 188.10 K) |
| Vapor pressure          | 4352 kPa at (21.1 °C)        |
| Viscosity               | 0.311 CP (-100 °C)           |

2.1.2 Sulphuric acid H₂SO₄

Sulphuric acid is a strong acid produced by the dissolving of sulphur trioxide in water.

\[
\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4
\]

Sulphuric acid is a colourless, viscous corrosive liquid which has a specification as shown in table2.
Table 2. The specification of sulphuric acid.

| Property            | Value                      |
|---------------------|----------------------------|
| Vapour pressure     | 0.001 mm Hg (20 °C)        |
| Viscosity           | 26.7 CP (20 °C)            |
| Odour               | odourless                  |
| Melting point       | 10 °C                      |
| Density             | 1.84 g/cm³                 |
| Boiling point       | 337 °C (610 K)             |
| Solubility in water | miscible                   |
| Molar mass          | 98.079 g/mole              |

3. RESULT AND DISCUSSION

3.1 Effect of Operating Time

The effect of operating time on permeate flux was studied in direct contact membrane distillation. When the feed containing initially 50g/dm³ HCl and 50g/dm³ H₂SO₄, and at temperature 333K as shown in Fig.2. Only hydrochloric acid gaseous and water vapor transferred through the membrane pores to the permeate during MD process but sulfuric acid remained in the feed and its concentration increasing gradually reached a value of 100g/dm³. Fig.2 show the changes in the concentration of HCl and H₂SO₄ with time. At the beginning of membrane distillation process both acids was gradually increase, because of only water vapor was transferred through the membrane, so HCl concentration slightly increase in the feed, this behaviour is agreement with Tomaszewska and Mientka, 2009. After one hour permeate concentration was 0.67g/dm³ but during 5 hours the permeate concentration increased to 1.8g/dm³, and the volume permeate flux was 71dm³/m².d from Eq(1).

3.2 Effect of Feed Concentration

When a higher concentration of HCl in the feed after the first hour the component appeared in the permeate of the concentration process, was 3.0991g/dm³ as shown in Fig.3, and during 5 hour permeate concentration reached 5.39g/dm³, and the volume permeate flux was 57.39dm³/m².d. When the initial concentration of sulphuric acid was equal to 161g/dm³ the permeate flux decrease to 35dm³/m².d as shown in Fig.4, these declines of volume permeate flux was caused by the decreasing in water vapour pressure being in equilibrium with the feed solution. When added non-volatile solute to solution caused decrease in water vapour pressure, this behaviour is agreement with Gryta, et al., 2001. The viscosity of the feed increase because of increase the concentration of sulphuric acid this is another factor, sulphuric acid has higher viscosity compared with another acids, so decrease the diffusivity. Diffusivity adversely related with viscosity, and also when the sulphuric acid weight present be higher than HCl caused a declines in HCl flux, this behaviour is agreement with Tomaszewska, et al., 1994.
3.3 Effect of Feed Temperature

In the case of acid mixture with the initial concentration $161\text{g/dm}^3$ $\text{H}_2\text{SO}_4$ and $60\text{g/dm}^3$ of $\text{HCl}$ at $343\text{K}$ the increase in feed temperature to $343\text{K}$ a faster concentration of sulphuric acid and hydrochloric acid on the feed side. In the membrane distillation process the initial composition of the feed, were the same as for temperature $333\text{K}$, the distillate consist of $\text{HCl}$ solution with higher concentration, due to the gas/liquid phase equilibrium. An elevation of temperature caused, higher partial pressure of volatile components, and large mass transfer of water vapour and $\text{HCl}$ across the membrane pores. The partial pressure of $\text{HCl}$ under these conditions was so high, that the volume permeate flux was twice higher than for $333\text{K}$, this behaviour is agreement with Tomaszewska and Mientka, 2009. And achieved a value $85.4\text{dm}^3/\text{m}^2.\text{d}$. The concentration of $\text{HCl}$ in the permeate achieved a value of $9.1\text{g/dm}^3$, this increases in $\text{HCl}$ concentration in the permeate caused by the water vapour was transferred through the membrane pores to the permeate with $\text{HCl}$ vapour, during the concentration of acids mixture containing of both $\text{HCl}$ and sulphuric acid the $\text{H}_2\text{SO}_4$ was completely retained on the feed side, this behaviour is agreement with Tomaszewska, et al., 1999. Thus its concentration constantly increased, as shown in Fig.5 can be seen, the increase of $\text{HCl}$ in the permeate due to an increase in the feed temperature. From the data initially the concentration of both acids were gradually increased at the beginning of MD process only water vapour was transferred across PVDF membrane. When the concentration of $\text{HCl}$ and sulphuric acid in the feed achieved the value of $71.35\text{g/dm}^3$ and $201.26\text{g/dm}^3$ respectively, the $\text{HCl}$ transfer through the membrane pores was noticed Fig.5. Large volume permeate flux in order to large mass transfer of water through the membrane.

The volume permeate flux is a function of feed temperature As shown in Fig.6. Due to an increase in feed temperature the volume permeate flux increase at the same concentration $111/61\text{g/dm}^3$, this behaviour is agreement with, Tomaszewska, et al., 1999. The volume permeates flux in MD with PVDF membrane was lower than permeate flux in case polytetrafluoroethylene (PTFE) membrane. The PVDF was thickener, which creates longer path way for vapour pressure diffusion. A change in membrane type causes a change in heat and mass transfer. There is a large difference in values of volume permeate flux between $333$-$343\text{K}$ feed temperature, as the temperature of the liquid increases due to the increasing in kinetic energy of the molecules, thus increasing vapour pressure. During the MD process of acids mixture $\text{HCl}$ gaseous transport through the membrane pores is too high, that mean that the concentration of $\text{HCl}$ in permeate is higher than in the feed under process conditions, as shown in Fig. 7. The final concentration of $\text{HCl}$ achieved in the permeate reached practically the same concentration in the feed and permeates were practically the same. From the data at temperature of the feed equal to $333\text{K}$ the concentration of $\text{HCl}$ in the permeate achieved a value of $3.0991\text{g/dm}^3$, but at temperature $339\text{K}$ achieved a value of $5.9\text{g/dm}^3$, and at temperature $343\text{K}$ achieved a value of $7.79\text{g/dm}^3$.  

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4. CONCLUSIONS

1. HCl permeate flux increase with an increase in concentration of HCl in the feed.
2. Volume permeates flux decrease with an increase in sulfueric acid concentration in the feed.
3. Feed temperature strongly influences on the permeate flux, volume permeate flux increase with an increase in feed temperature.

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**Figure 1.** Schematic diagram of MD process.
Figure 2. Gradual concentration of HCl/H$_2$SO$_4$ model solution by MD at feed temperature 333k, CHCl/CH$_2$SO$_4$ = 50/50 g/dm$^3$.

Figure 3. Gradual concentration of HCl/H$_2$SO$_4$ model solution by MD at feed temperature 333k, CHCl/CH$_2$SO$_4$ = 111/61 g/dm$^3$. 
Figure 4. Gradual concentration of HCl/\(H_2SO_4\) model solution by MD at feed temperature 333 K, \(CHCl/C\ H_2SO_4=60/161\ g/dm^3\).

Figure 5. Gradual concentration of HCl/\(H_2SO_4\) model solution by MD at feed temperature 343K, \(C\ HCl/C\ H_2SO_4=60/161\ g/dm^3\).
Figure 6. The effect of temperature on volume permeate flux at a feed concentration $C_{HCl}/C_{H_2SO_4} = 111/61 \text{ g/dm}^3$.

Figure 7. The effect of temperature on HCl concentration in the permeate at a feed concentration of $C_{HCl}/C_{H_2SO_4} = 111/61 \text{ g/dm}^3$. 
Figure 8. The ionic content test of the permeate at a feed concentration of 50/50 g/dm³.