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EXPERIMENTAL AND MATHEMATICAL MODELING STUDIES OF LIQUID-LIQUID MEMBRANE CONTACTOR

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Abstract

Experimental and modeling studies of the effect of temperature on liquid-liquid membrane contactor (LLMC) have been done. The experiments were conducted by varying temperature of 25 up to 80°C, cross flow velocity from 0.02 to 0.05 m/s and feed concentration of 0, 5000 and 30000 mg/L. In these experiments microporous hydrophobic hollow fiber polypropylene membrane with 0.2 μm was used as a contacting device. The modeling has been done by compiling mathematic equations of mass and heat transfers in liquid-liquid membrane contactor. Both the experimental and modeling results show, the increase in feed temperature increases the flux of pure water exponentially, whereas the flux decreases with increasing the permeate temperature. The feed temperature increase at higher temperature result in higher flux increases. The concentration of pure water resulted in the range of 1.8 to 5.6 mg/L depending on feed concentration.

Key words : *membrane contactor, modeling*

Introduction

The limitation of fresh water which can be used by man cause there have been chronic water shortages especially in coastal and remote areas. Ninety seven percents of all the earth's water is salty availabled in the oceans and lakes (Takenaka Corp., 2001). Currently, implemented technologies for converting seawater into freshwater have been developed. These technologies were inisialised by multieffect distillation, vapor compression, solar distillation up to membrane technology. One of membrane technologies which has high potential for drinking and/or pure water production from seawater or brackish water especially for small and medium scale is liquid-liquid membrane contactor (LLMC).

LLMC is a membrane separation using hydrophobic microporous membranes. Due to their hydrophobicity the liquid cannot penetrate into membrane pores, but the vapour can pass the pores by applying a vapour pressure difference. The process scheme of liquid-liquid membrane contactor is shown in Figure 1.(Scarab, 1999). In this process, the distillation is performed at ambient pressure and at maximum temperature of 90°C. Operating costs are extremely low because the process can be driven by low temperature heat source eg. solar heat or waste heat (Bier,C. and Plantikow,U., 1995; Scarab, 1999; Takenaka Corp., 2001 ; Shcofield, R.W. et.al, 1990). Researches to increase LLMC performance have been done (Drioli and Wu, 1985; Lawson,K.W. et.al., 1998; Kubota, S. et al, 1998; Schneider,K. et.al, 1985). To gain better understanding of the effect of temperature on LLMC performance was investigated in this paper by experimental and modeling. The model was then compared with the experimental results in respect to the effect of temperature on flux.

Figure 1. explains that, temperature is one of the process variable which strongly affects the LLMC performance. Theoretically the increase of feed temperature increases the vapour pressure as the driving force transport process.

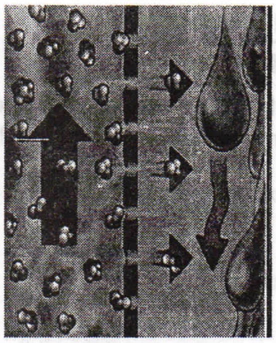

Figure 1. Schematic representation of LLMC

Mathematical modeling

Mathematical modeling was performed to predict the flux theoretically based on mass and heat

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transfers. The schematic of transport process of vapour from feed to side permeate side in this paper is shown in Figure 2.

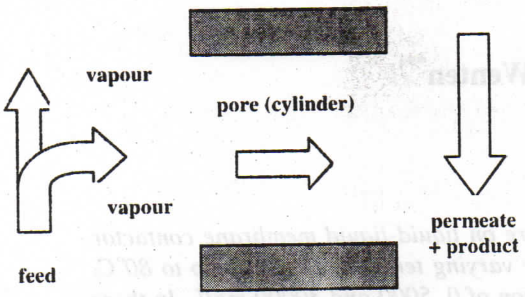

Figure 2. Schematic of mathematical modeling

Mass transfer of water vapour within the membrane pores can be describe as movement of water vapour molecules in long channel with cylinder shape. Evaporation initialized from contact area between vapour and membrane surface on feed side, afterwards move to contact area between water vapour and water cooler on permeate side.

Resistance to mass transfer comes from both the membrane structure and the presence of air trapped within the membrane (Schofield, 1987). The describe by either the Knudsen diffusion model or Poiseuille model, the later being dominant when the membrane pore size is larger than the mean free molecular path of gaseous water molecule.

The mass transfer from the Knudsen diffusion model may be expressed as :

$$J_K = \frac{2}{3}\frac{r\varepsilon}{\chi}\left\{\frac{8RT}{\pi M}\right\}^{0.5}\frac{M}{RT}\frac{\Delta P}{\delta} \qquad (1)$$

The Poiseuille flow model is based on viscous flow through a capillar, and can be expressed as :

$$J_P = \frac{1}{8}\frac{r^2\varepsilon}{\chi}\frac{1}{\mu}\frac{MP}{RT}\frac{\Delta P}{\delta} \qquad (2)$$

while mass flux through a stationary film of air can be described by the molecular diffusion model :

$$J_D = \frac{1}{P_a}\frac{\varepsilon}{\chi\delta}\frac{DM}{RT}(P_f - P_p) \qquad (3)$$

$$J_D = \frac{d}{P_a}\Delta P$$

In equation (3) the value of Pa can be calculated with equation :

$$P_a = P_{liq} - \left(\frac{P_f + P_p}{2}\right) \qquad (4)$$

Many models have been developed for describing mass transport process that considers the preceding models. In this research Knudsen/Poiseuille transition region model was formulated, to describe resistance by membrane structure. Inspection of equations (3) and (4) revealed that in Knudsen $J \propto \Delta P$, while in Poisseulle flow, $J \propto P\Delta P$. This lead to equation:

$$J = a\,\wp^b\,\Delta P \qquad (5)$$
$$0 < b < 1$$

where $\wp$ = dimensionless pressure = P/P_{ref}
a = membrane permeation constant
b = fraction of permeability arising from viscous effects
= 0 for Knudsen diffusion
= 1 for Poisseuille flow

The reference pressure, P_{ref}, is a typical or average water vapour pressure for the system, for example 25 kPa for low temperature LLMC. The membrane permeation constant, a, is simply proportional between flux and pressure drop at the reference pressure. The exponent b, indicate the extent to which viscous effect control the process.

Equation (3) is applicable to aerated LLMC systems, while equation (5) applies to fully deaerated systems. For partially deaerated systems, as would often be the case, combination of the two mechanism are essentially independent, the approach used here is to add the resistance imposed by both models, giving

$$J = \left\{\frac{1}{a\,\wp^b} + \frac{Pa}{d}\right\}^{-1}\Delta P \qquad (6)$$

Thus three parameters, a, b, and d, are required to predict LLMC fluxes at any pressure, Pa, remembering that $\wp$ and ΔPrefer to water vapour pressure only.

Heat transfer occurs by two mechanisms, latent heat transfer that elaborate vapour flux and conductive transfer through membrane. The mechanisms include : (1) heat transfer is transported to the membrane interface by means of a film heat transfer coefficient, h_f, where the subscript f refers to the feed. (2) similarly, heat is removed by permeate subject to the film heat transfer coefficient h_p. (3) and (4) this heat passes across the membrane by two parallel paths, namely vaporization and conduction, as described by the two heat transfer coefficients h_v and the h_c respectively.

The value of latent heat flux that occurs is a heat, used for evaporating mass flux is :

$$Q_v = J\Delta H_v = h_v\Delta T_m \qquad (7)$$

While the heat transfer by conduction across the membrane is given by the equation

$$Q_C = km\,\Delta T_m/\delta \qquad (8)$$
$$= hc\,\Delta T_m$$

where $k_m = \varepsilon\,kg + (1-\varepsilon)\,ks$.

The heat fluxes across the membrane are adding the latent heat transfer and conductive transfer. These heat flows can be added linearly to give the total heat flux.

$$Q = Q_V + Q_C \quad (9)$$
$$= (h_c + h_v)\,\Delta T_m$$

From equation (7), vapour heat transfer coefficient can be calculated with equation :

$$h_v = \frac{J\Delta H_v}{(T_{fm} - T_{pm})} \quad (10)$$

Temperature on membrane surface T_{fm} and T_{pm} depend on feed temperature (T_f), permeate temperature (T_p) and heat transfer coefficient. This relationship given with equation :

$$T_{fm} = T_f - (T_f - T_p)\frac{\frac{1}{h_f}}{\frac{1}{(h_v + h_c)} + \frac{1}{h_f} + \frac{1}{h_p}} \quad (11)$$

$$T_{pm} = T_p + (T_f - T_p)\frac{\frac{1}{h_p}}{\frac{1}{(h_v + h_c)} + \frac{1}{h_f} + \frac{1}{h_p}} \quad (12)$$

In LLMC occurs the reducing of temperature from feed side, T_f to T_{fm} at the membrane surface and then continued reducing temperature from membrane surface T_{pm} to T_p as permeate temperature. This phenomenon indicates temperature polarization. Temperature polarization cause heat transfer inefficient, hence has to avoid. Temperature polarization can be quantified by means of a temperature polarization coefficient, τ defined as the fraction of the overall driving force that contribute to the trans-membrane driving force.

$$\tau = \frac{T_{fm} - T_{pm}}{T_f - T_p} = \frac{h}{(h + h_c + h_v)} \quad (13)$$

Where,

$$h = \left(\frac{1}{h_f} + \frac{1}{h_p}\right)^{-1}$$

For most application of LLMC, combination of heat and mass transfer equation is sufficiently complex to justify computer modelling and iterative solution, rather than direct solution of the equations. For this simplified case, the heat and mass transfer equation can be combined to give :

$$J = \frac{h_v}{\Delta H_v}\,\frac{h}{h_v + h_c + h}\,(T_f - T_p) \quad (14)$$

Where

$$h = \left(\frac{1}{h_f} + \frac{1}{h_p}\right)^{-1} = \frac{h_f}{2}$$

If

$$h_v = \Delta H_v \frac{dP}{dT}\left\{\frac{1}{a\wp^b} + \frac{Pa}{d}\right\}^{-1}$$

$$h_c = \{\varepsilon k_g + (1-\varepsilon) k_s\}/\delta$$

$$C = \left[\frac{1}{a\wp^b} + \frac{Pa}{d}\right]^{-1} \quad \text{so,}$$

$$h_v = \Delta H_v\, C\, \frac{dP}{dT} \quad (15)$$

Theoretically flux can be obtained by solving the mass and heat transfers model simultaneously. Successive substitution method is used to solve the mathematical models. Algorithm of solution is shown in Appendix A. The MATLAB program is used to support this method.

Experimental

Microporous hydrophobic hollow fiber polypropylene membrane with pore size of 0.2 µm was used as a membrane material. NaCl aqueous solution and pure water were used as feed and permeate respectively. The effect of feed and permeate temperature on flux and product quality were studied by varying the temperature from 25 to 80°C. The experimental apparatus set ups in this study is shown in Figure 3.

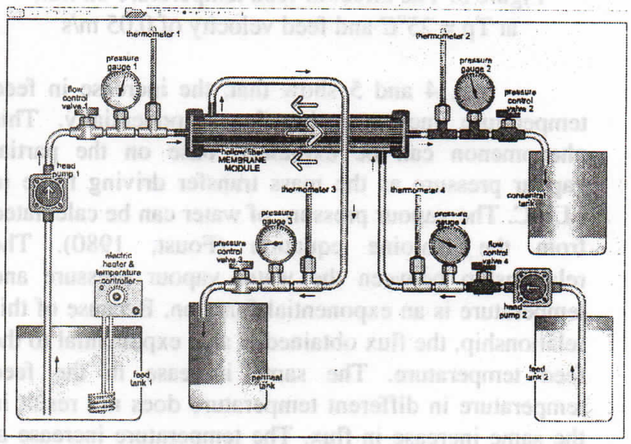

Figure 3. Schematic of experimental apparatus set ups

Result and Discussion

The effect of feed temperature on flux

The feed temperature is a process variable which strongly affects the flux of LLMC very much. In this experiment the feed temperature is varied from 40°C to 80°C. The permeate temperature at this study is 25°C. The experimental results are shown in Figure 4 and 5.

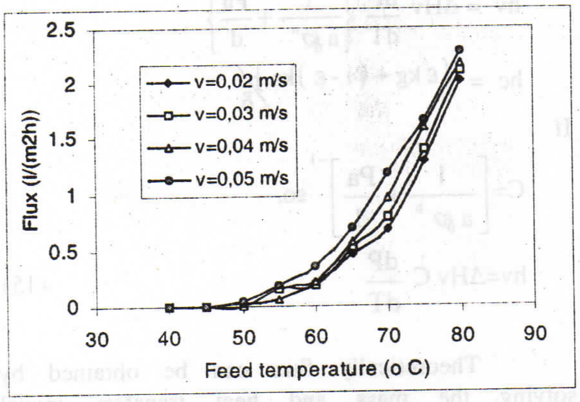

Figure 4. The effect of feed temperature on flux at Tp = 25°C and NaCl = 30000 mg/L

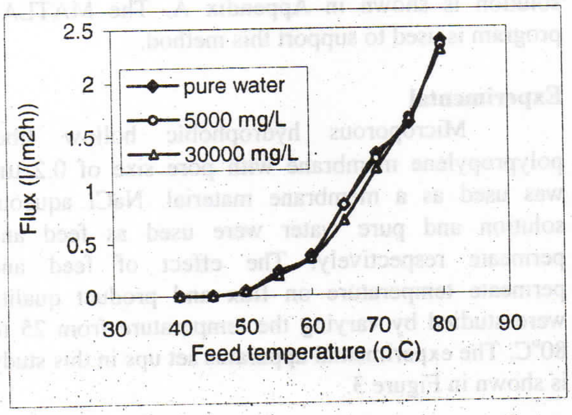

Figure 5. The effect of feed temperature on flux at Tp = 25°C and feed velocity of 0,05 m/s

Fig. 4 and 5 show that, the increase in feed temperature increases the flux exponentially. This phenomenon can be explained base on the partial vapour pressure as the mass transfer driving force in LLMC. The vapour pressure of water can be calculated from the Antoine equation (Foust, 1980). The relationship between the water vapour pressure and temperature is an exponential function. Because of this relationship, the flux obtained is also exponential to the feed temperature. The same increase in the feed temperature in different temperature does not result in the same increase in flux. The temperature increase at higher temperature result in higher flux increases. For example, the flux increase caused by the increase in feed temperature from 70°C to 80°C is 1.101 l/(m^{2}h), whereas at the increase of flux by the increase of feed temperature from 50°C to 60°C is 0.31 l/(m^{2}h).

The effect of permeate temperature on flux

The permeate fluid has an important role in providing the driving force of the transport in LLMC. Because of that, the permeate temperature determines the flux obtained. The permeate temperature was varied from 25, 30 and 35 °C to study the effect of permeate temperature on flux. The concentration of solute, which was used, is 30000 mg/L and cross flow velocity 0.05 m/s. The experimental result is depicted in Figure 6.

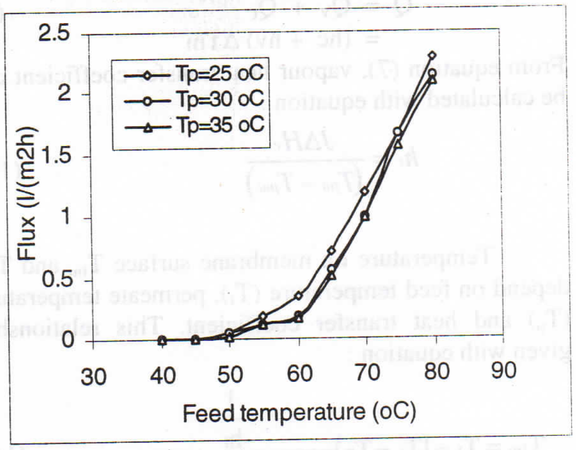

Figure 6. The effect of permeate temperature on flux at NaCl 30000 mg/L and feed velocity of 0.05 m/s

It is shown that, the lower the permeate temperature the higher the flux. This is caused by the higher vapour pressure difference is resulted at lower permeate temperature. However, the flux difference at the permeate temperature of 25, 30 and 35 °C is not significant. This is due to the very small difference in water vapour pressure at these temperatures. For example, the vapour pressure at temperature of 25°C is 3.153 kPa and at temperature 35 °C is 5.616 kPa, whereas the temperature of 80 °C is 47.439, therefore the vapour pressure difference resulted by the increase of permeate temperature from 25-35°C is relatively constant.

The effect of bulk temperature difference on flux

The effect of temperature on flux can also be demonstrated by varying the difference between bulk temperature of feed (Tf) and permeate (Tp). In this experiment, permeate temperatures were varied over a wide range to give bulk temperature difference from 10 to 55°C to understand the effect of bulk temperature difference on flux. The experiment was done at the feed temperature 80 °C and feed velocity 0.05 m/s. The experimental result is shown in Figure 7.

Figure 7 shows that, the increase in bulk temperature difference increases the flux. The higher the bulk temperature difference the higher the vapour pressure difference, and thus higher flux will be achieved. At the bulk temperature difference of more than 40 °C, the flux is relatively constant. This phenomenon can be explained by explaining the driving force that causes the transport. At the bulk temperature difference more than 40 °C, the difference of vapour pressure relatively constant, consequently the flux relatively constant too. The flux, which is obtained, will be different for the different feed temperature, despite having the same bulk temperature difference.

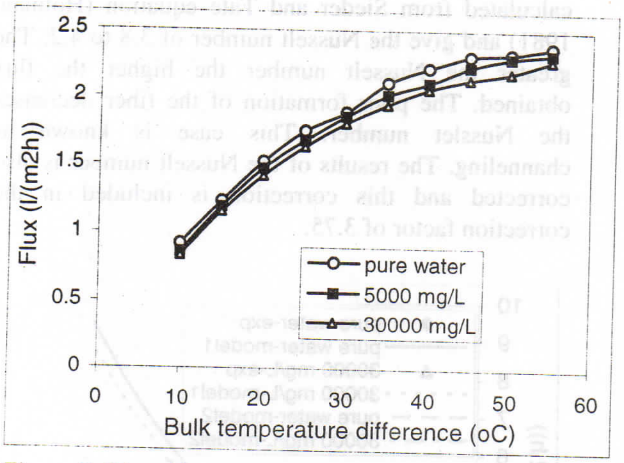

Figure 7. The effect of bulk temperature difference on flux at Tf= 80°C and feed velocity 0.05 m/s

The effect of feed temperature on product quality

Other than the flux, the product quality is an indicator, which can be used as a judgment of LLMC performance. To understand product quality in LLMC, experiments were conducted by varying the feed temperature at the feed concentration 5000, 30000 and 100000 mg/L. The permeate temperature and the feed velocity are 25°C and 0.05 m/s respectively. The experimental result is shown in Figure 8.

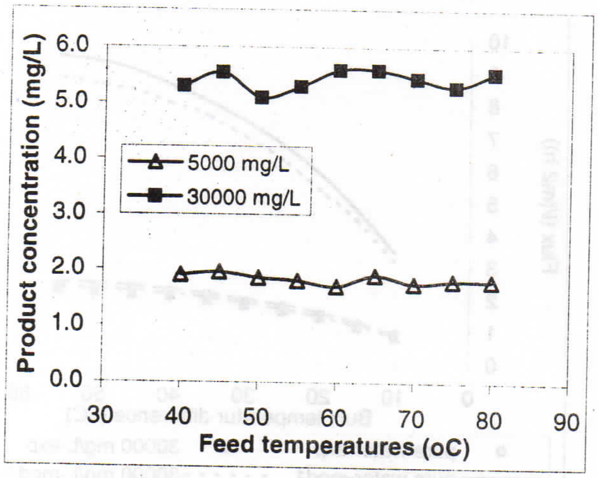

Figure 8. The effect of feed temperature on product quality at permeate temperature of 25°C and feed velocity of 0.05 m/s

From Fig. 8, it can be explained that, the increase in feed temperature doesn't influence the product quality. This phenomenon show that, an influence can be achieved by the membrane material used alone. The membrane material used is polypropylene, which is a hydrophobic material. This hydrophobicity will prevent the liquid penetration into the membrane pores, so that the product quality only depend on water vapour quality, which is evaporated at the membrane surface. The product quality of pure water are 2 mg/L for feed concentration 5000 mg/L and 5.4 mg/L for feed concentration 30000 mg/L.

Mathematical Modeling

Mathematical modelling is compiled to predict the flux theoretically. The model was compiled base on heat and mass transfers. The parameters examined are the temperature, the feed velocity and the feed concentration. The results of the model were compared with the experiment results are shown in Figure 9 and Fig. 10.

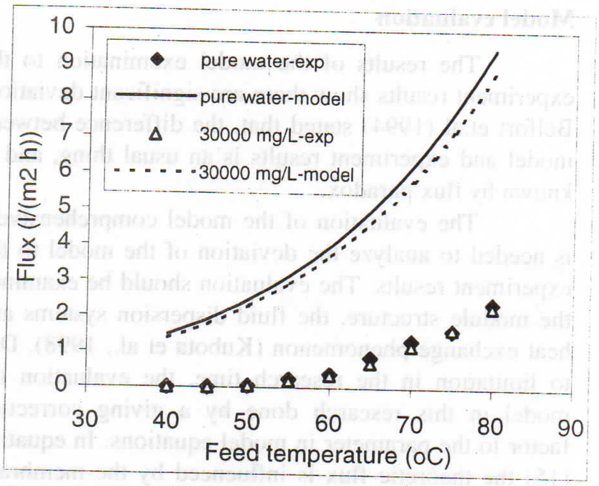

Figure 9. Modelling and experiment the effect of feed temperature on flux, at Tp = 25°C and v = 0.05 m/s

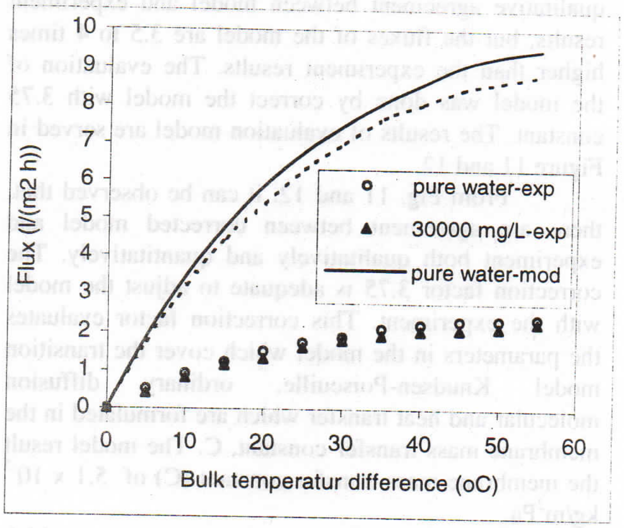

Figure 10. Modelling and experiment the effect of bulk temperature difference on flux at Tp = 25°C and v = 0.05 m/s

Fig. 9 seems both the experiment and model results show that, The increase in feed temperature increases the flux exponentially. Figure 10. seems both the experiment and model results, the increase in bulk temperature difference increases the flux until the temperature difference 40°C.

In general, both Fig.9 and 10 show that, there are quantitative difference between model and experiment results, but the model results agree to the experiment result qualitatively. These phenomena are caused by the treatments which are used in compilation of model. In compilation the model is used the ideal conditions which are formulated in assumptions. This condition will cause the higher fluxes are obtained in the model than the experiment results. On the other hand the experiments were done by the membrane module, which was not worked on a well machine design, consequently the performance of the module is imperfect. These conditions lower the fluxes obtained.

Model evaluation

The results of the model examination to the experiment results show there are significant deviation. Belfort et.al (1994) stated that, the difference between model and experiment results is an usual thing, and is known by flux paradox.

The evaluation of the model comprehensively is needed to analyze the deviation of the model to the experiment results. The evaluation should be examined the module structure, the fluid dispersion systems and heat exchange phenomenon (Kubota et al., 1998). Due to limitation in the research time, the evaluation the model in this research done by a giving correction factor to the parameter in model equations. In equation (15) the theoretic flux is influenced by the membrane mass transfer constant, C.

Figure 9 and 10 show that, there are qualitative agreement between model and experiment results, but the fluxes of the model are 3.5 to 4 times higher than the experiment results. The evaluation of the model was done by correct the model with 3.75 constant. The results of evaluation model are served in Figure 11 and 12.

From Fig. 11 and 12, it can be observed that, there are agreement between corrected model and experiment both qualitatively and quantitatively. The correction factor 3.75 is adequate to adjust the model with the experiment. This correction factor evaluates the parameters in the model which cover the transition model Knudsen-Poiseuille, ordinary diffusion molecular and heat transfer which are formulated in the membrane mass transfer constant, C. The model result the membrane mass transfer constant (C) of 5.1×10^{-7} kg/m^{2}Pa.

In diffusion molecular, the parameters which are corrected are porosity (ε), tortuosity (χ) and membrane thickness (δ). Model simulations were done by using the porosity of 70%, the tortuosity of 1 and the membrane thickness of 150 µm. In the transition model Knudsen-Poiseuille region, beside the parameters have been mentioned, the correction factor is also used to evaluate the pores size, the mean free path of gas and the mean molecular speed. The observation in module structure, the formation of the fibers in shell side determine the Nusselt number (Nu). The model simulations were done with the Nusselt number calculated from Sieder and Tate equation (Holman, 1981) and give the Nusselt number of 3.8 to 4.2. The greater the Nusselt number the higher the flux obtained. The poor formation of the fiber decreases the Nusslet number. This case is known as channeling. The results of the Nusselt number is also corrected and this correction is included in the correction factor of 3.75.

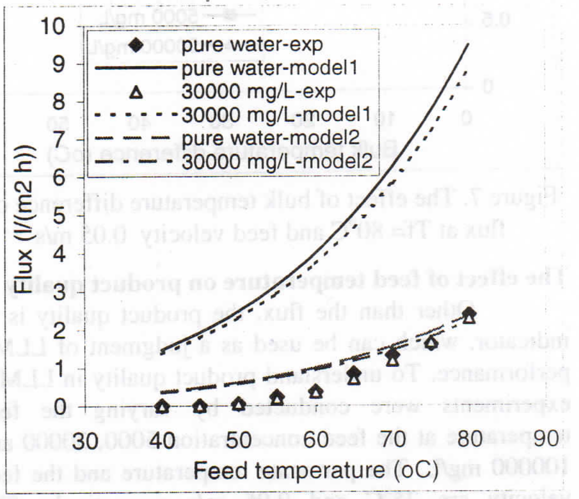

Figure 11. Model evaluation the effect of feed temperature on flux at Tp = 25°C dan v = 0.05 m/s

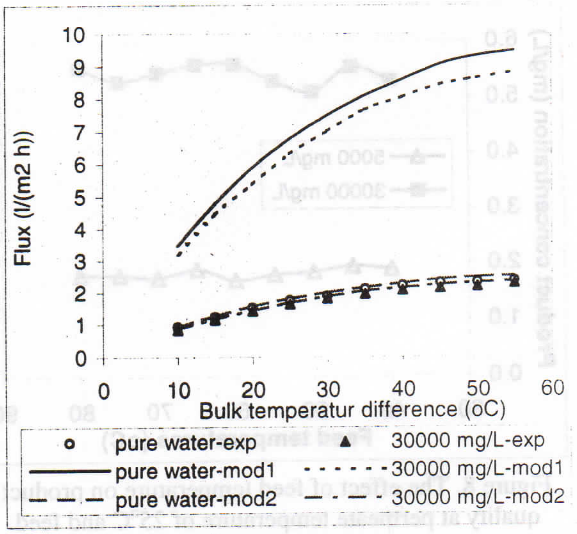

Figure 12. Model evaluation the effect of bulk temperature difference on flux, atTp = 25°C dan v = 0,05 m/s

Conclusion and Recommendation

The studiy of the effect of temperature on LLMC performance has been done. Both the experimental and modeling results show, the increase in feed temperature increases the flux of pure water exponentially, whereas the flux decreases with increasing the permeate temperature. The feed temperature increase at higher temperature result in higher flux increases. The concentration of pure water resulted in the range of 1.8 to 5.6 mg/L depending on feed concentration. The results of model simulation show that, there are quantitative difference between model and experimental results, but the model agree to the experimental result qualitatively. The correction factor of 3.75 is adequate to adjust the model with the experiment both quantitatively and qualitatively.

The studies of the effect of temperature on LLMC performance have been done, however the flow regions which are laminar conditions. Therefore, it is recommended to investigate the performance of this process under turbulent conditions. The comprehensive evaluation is needed to analyze the deviation between model and experiment results. The evaluation should examin the module structure, the fluid dispersion systems and heat exchange phenomenon. In addition, well prepare module to accommodate better hydrodynamic system is needed to evaluate the model.

Notations

a : membrane permeability constant [kg/(m s Pa)]
b : fraction of permeability arising from viscous effect [-]
c : feed concentration [mg/dm^3, kg/m^3]
C : membrane mass transfer constant [kg/(m^2 s Pa)]
Cp : heat capacity [J/(kg K)]
d : membrane molecular diffusion constant[kg/(m^{2}s)]
d_h : hydraulic diameter [m]
D : diffusion coefficient [m^2/s]
ΔH_v : latent heat of vaporization [J/kg]
h : heat transfer coefficient (overall) [W/(m^{2}K)]
J : mass flux through membrane [kg/(m^{2}jam)]
k : thermal conductivity [W/(m^{2}K)]
k_s : solute mass transfer coefficient [m/s]
M : molecular weight [kg/mol]
n : number of fiber [-]
N_u : Nusselt number [-]
P : water vapour pressure [Pa]
P^o : pure water vapour pressure [Pa]
p : wetted perimeter [m]
$\wp$: dimensionless pressure = P/Pref [-]
Q : heat flux [W/m^2]
r : pore radius [m]
R : Gas constant [J/(mol K)]
T : temperature [K, ^{o}C]
v : feed velocity (m/s)
σ : surface tension [N/m]
τ : temperature polarization coefficient [-]
x : mole fraction of slolute [-]
α : module shell side void fraction [-]
δ : membrane thickness [m]
ε : membrane porosity [-]
μ : gas viscosity [Pa s]
ρ : density [kg/m^3]
χ : membrane tortuosity [-]
γ : activity coefficient [-]

Subscripts

a : air
c : conduction
f : feed
fm : membrane surface of feed side
p : permeate
pm : membrane surface of permeate side
g : gas
liq : liquid
m : membrane
s : solid
v : vapour
D : diffusion molecular
K : Knudsen
P : Poieseuille
w : water

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Appendix A
Algorithm for execution of mathematical model