Influence of Temperature Drop by Phase Transition on Pervaporation Processes in Vapor Phase Feed

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Abstract−In this study, pilot pervaporation experiments of ethanol dehydration from the vapor phase feed have been carried out. The dehydration time decreased with increasing of the feed temperature and did not vary with the feed flow rate. The temperature dependence of permeation rate in vapor phase feed was larger than that in liquid phase feed. Contrary to the pilot pervaporation of liquid phase feed, the higher the feed flow rate, the larger the temperature drop is. The variation of temperature drop with permeate flux in vapor phase feed is larger than that in liquid phase owing to the heat loss of the membrane module itself.

Key words: Pervaporation, Temperature Drop, Flow Rate, Heat Loss, Phase Transition

INTRODUCTION

Pervaporation is a membrane process used for the separation of liquid mixtures by means of partial vaporization across a permselective membrane. The permeate is then obtained as a liquid by condensation. The driving force for permeation is established by maintaining a difference in the partial pressure of the permeate across the membrane. This is accomplished in vacuum pervaporation by lowering the total pressure on the downstream side of the membrane [Yeom et al., 1996; Chang et al., 1998].

Pervaporation differs from other membrane processes, because the process includes a phase change or vaporization step of the permeate. The vaporization enthalpy of the feed liquid must be supplied from a sensible heat of the feed under adiabatic conditions. Hence, the temperature of the retentate will be dropped during this process. According to the solution-diffusion model [Wijman and Baker, 1995], sorption rate of permeate onto the membrane, diffusivities of the permeate inside the membrane and the driving force of pervaporation can be affected by temperature drop. Therefore, the overall selectivity and permeate flux will be changed considerably with the temperature drop, which may not be observed in other membrane processes without phase transition. If correlations obtained from other membrane processes without phase transition are applied to the pervaporation process without any modification, incorrect results are estimated.

The temperature drop is not easy to detect in small-scale pervaporation experiments, because the pervaporation module is submerged in a constant-temperature condition and its area is too small. Thus, the enhancement of mass transfer rate by increasing flow rate can be misinterpreted as the boundary layer effect. However, it becomes generally known that the temperature drop affects mass transfer rate in pilot pervaporation. Due to the large area and high flux of the membrane, the module temperature is difficult to maintain constant. Rautenbach and Albrecht [1980, 1985] calculated the temperature drop at the membrane interface in a water/cellulose acetate system. Depending on the flow conditions, a temperature drop between 5 K and 12 K was expected. They predicted the temperature profile through the simulation of the transport equations proposed by Greenlaw et al. [1977].

There have been many researches concerned with the pervaporation process recently, but most of them have concentrated on the mass transfer and separation mechanism. However, only a few papers are related to the heat transfer aspect of pervaporation [Rautenbach and Albrecht, 1980, 1985; Rautenbach et al., 1991; Ito et al., 1997; Olsson and Tragardh, 1999].

In this study, the temperature drop during hydration of ethanol in pilot pervaporation unit was measured. The effects of inlet temperature, feed flow rate and feed ethanol concentration on temperature drop were studied. The feed phase in this study was vapor, and the results in liquid feed have already been reported [Song et al., 1996].

THEORY

1. Heat Supply Ratio and Heat Transition Ratio

In the pervaporation process, the evaporation of the permeate is an essential step. The heat flux for phase transition of the permeate is as follows [Rautenbach and Albrecht, 1985]:

$$Q=P(\Delta H_v + C_p^p \Delta T) \tag{1}$$

where P is the permeation flux and ΔT is the temperature drop through the membrane or between inlet and outlet feed flow. C_p^p and ΔH_v are the heat capacity and the heat of evaporation, respectively. In this equation, it can be assumed that variation of enthalpy in the vapor phase is negligible. The heat flux is necessary for the phase change at the membrane surface to the permeate compart-

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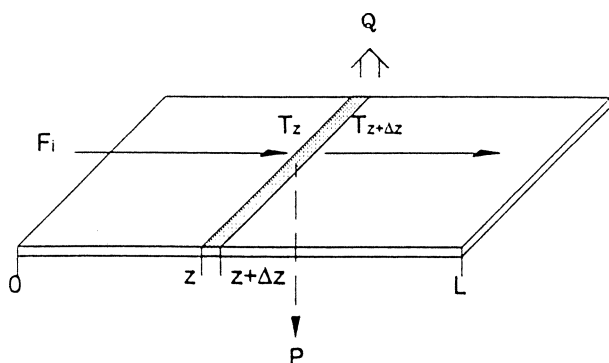E-mail: whhong@mail.kaist.ac.kr

Fig. 1. Heat balance for pervaporation.

ment, and temperature gradients develop orthogonally to the membrane as well as in the direction of flow.

The heat balance for pervaporation is illustrated in Fig. 1. When the heat of evaporation is supplied only from the permeate itself and there is no heat supplement from the environment, Q is zero in Eq. (1). And in the case of heat supply from the permeate itself, temperature gradients by phase transition of permeate develop across the membrane. Therefore, the following energy balance is applied:

$$PC_p^p \Delta T_y = -P \Delta H_v \tag{2}$$

where ΔT_y is the temperature difference orthogonal to the membrane.

Rautenbach and Albrecht [1985] observed 5-12 K temperature drop through the membrane ΔT_y and the temperature drop was increased with decreasing of the feed flow rate.

If the heat of evaporation is supplied only from the feed mixture, a temperature gradient develops mainly in the direction of feed flow. When the pressure difference between the permeate and the retentate is not large, the expansion heat under isothermal conditions can be neglected. Therefore, the following energy balance is established from Eq. (1):

$$\rho^f FC_p^f \Delta T_z = -P A_p \Delta H_v \tag{3}$$

where F is the feed flow rate and A_p is the surface area of the membrane. The temperature drop between inlet and outlet flow, ΔT_z, is expressed by:

$$\Delta T_z = -\frac{P A_p \Delta H_v}{\rho^f FC_p^f} \tag{4}$$

However, the vaporization enthalpy required for permeate is actually supplied from both the permeate and the retentate. When the expansion heat under isothermal condition is neglected, the energy balance in real pervaporation operation is written finally as:

$$\frac{\rho^f FC_p^f \Delta T_z}{A_p} + PC_p^p \Delta T_y = -P \Delta H_v \tag{5}$$

The cut ratio θ proposed by Rautenbach and Albrecht [1980] can be expressed as follows:

$$\theta = -\frac{C_p^p \Delta T_y}{\Delta H_v} \tag{6}$$

In this research the cut ratio θ is defined as heat transition ratio, which means the ratio of vaporization enthalpy supplied by the per-

meate. And heat supply ratio ϕ of vaporization enthalpy taken from the retentate is defined as follows [Song et al., 1996]:

$$\phi = -\frac{\rho^f FC_p^f \Delta T_z}{P A_p \Delta H_v} \tag{7}$$

In Eqs. (6) and (7), $-\Delta H_v/C_p^p$ and $-P A_p \Delta H_v/\rho^f FC_p^f$ are the maximum permissible temperature drop of the permeate and the retentate, respectively.

The heat transition ratio means the relative amount of energy supplied from the the permeate itself for evaporation. When ΔT_y has a maximum value, the heat transition ratio becomes 1, which means that the vaporization enthalpy is only supplied by the permeate itself. When the heat of evaporation is supplied totally by the retentate, the heat supply ratio becomes 1 and ΔT_z has a maximum value. Therefore Eqs. (6) and (7) can be converted into the following equations:

$$\theta = \frac{\Delta T_y}{(\Delta T_y)_{max}} \tag{6a}$$

$$\phi = \frac{\Delta T_z}{(\Delta T_z)_{max}} \tag{7a}$$

The main operating variables in pervaporation are feed concentration, feed flow rate, feed temperature, and downstream pressure [Hong and Hong, 1999]. Eqs. (6) and (7) show that, among these variables, feed flow rate and temperature are major operating variables influencing heat supply ratio. The feed flow rate affects the resistance in the boundary layer, and the feed temperature influences the flux and the selectivity for a given membrane. The heat supply ratio contains the operating conditions such as F and T_{feed}, which can be easily calculated from experimental data; therefore, the heat supply ratio is more convenient to use than the heat transition ratio.

2. Phase Transition of Retentate

In case of liquid feed, the increase of feed flow rate reduces the temperature drop within the pervaporation module. The mass transfer rate decreases with increasing temperature drop. In case of vapor feed, since the heat of evaporation can be supplied by the phase transition of the retentate, we can observe the different phenomenon of insignificant temperature drop. In this case the energy balance can be written as:

$$\phi P A_p \Delta H_v^p = \rho^f F(q \Delta H_v^f - C_p^f \Delta T_z) \tag{8}$$

$$\Delta T_z \leq T_{feed} - T_b \tag{8a}$$

where q is a fraction of phase transition of the retentate to liquid. Assuming $T_{feed} \approx T_b$, the amount of energy supply calculated by the temperature change of the retentate is negligible. Thus,

$$\phi P A_p \Delta H_v^p = \rho^f q F \Delta H_v^f \tag{9}$$

where qF is the amount of the retentate of the phase transition from vapor to liquid, and it can be rewritten as the following:

$$qF = F^v \big|_{inlet} - F^v \big|_{outlet} = \frac{\phi P A_p \Delta H_v^p}{\rho^f \Delta H_v^f} \tag{10}$$

EXPERIMENTAL

1. Apparatus

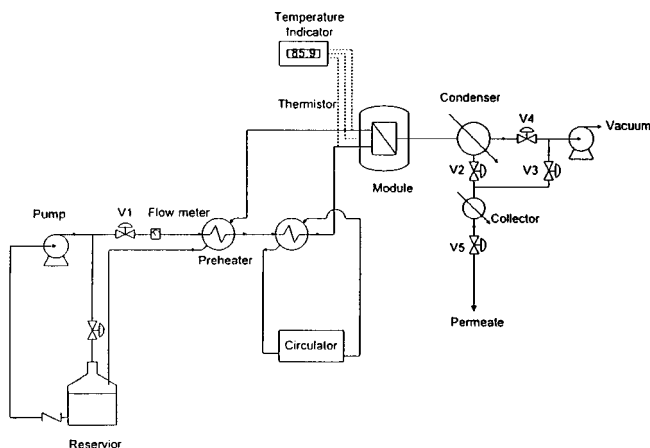The pilot pervaporator used in this study is a PERVAP® separa-

Fig. 2. Schematic diagram of pilot pervaporation unit.

tor (Carbone Lorraine Co.). Fig. 2 is a schematic diagram for the pervaporation experimental apparatus. The module installed in the pervaporator is the plate and frame type and the effective area of the membrane is 1 m². The thickness of the membrane is about 200 μm, but the thickness of the active layer is 0.1-2 μm according to the manufacturer. The number of channels is 11 and the gap is 0.1 cm.

2. Material and Experimental Condition

The concentration of the ethanol feed mixture is about 93 wt% and the total amount fed into the reservoir is about 15 L. The measured feed temperatures are 67, 71, 76, 79, 81 and 83 °C. The feed flow rates are 20, 40, 60 and 80 L/hr. The Reynolds number does not exceed 10. The state of the feed at 79, 81 and 83 °C is vapor. The condenser and the collector are maintained at 0 °C. The concentration of retentate and the amount of permeate are measured. The selectivity and the flux are calculated from these results. The temperatures at inlet and outlet are measured by a thermistor which can be read to 0.01 °C.

3. Theoretical Calculation

The permeation rate P was expressed as a function of temperature [Neel, 1991; Karlsson and Tragardh, 1993] and used in order to calculate the temperature profile. The temperature profile was calculated by the equations suggested by Song et al. [1996].

$$P = P_0 \exp\left(-\frac{\Delta E}{RT}\right) \quad (11)$$

where P_0 and ΔE are measured through the experiments. The IMSL subroutine of the Gauss-Kronrod equation is applied in this procedure. The calculation conditions are derived from the operating conditions of the real pilot pervaporation. The heat supply ratio is 0.3, 0.5, 0.7 and 0.9, whose values are selected through the experimental results. The temperature drop caused by the heat loss is changed as the operating condition, but we chose 7 °C obtained at 76 °C and 20 L/hr in order to compare with the results calculated at the same condition.

RESULTS AND DISCUSSION

1. Dehydration of Ethanol in the Case of Vapor Feed

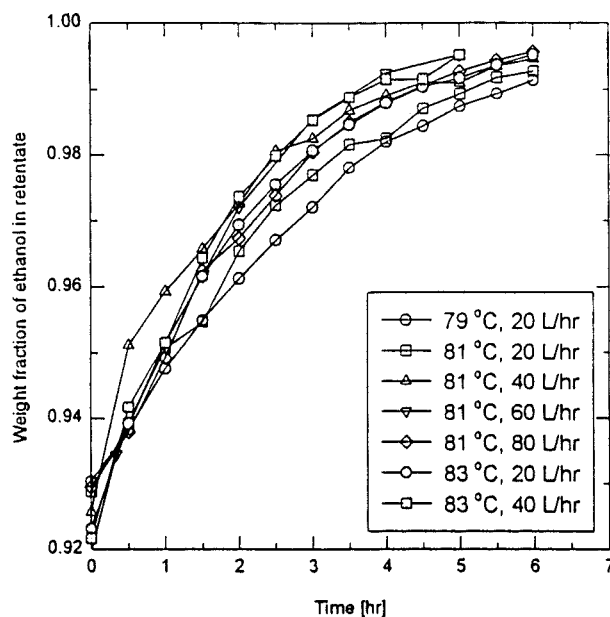Fig. 3 illustrates the ethanol concentration of retentate with oper-

Fig. 3. Ethanol concentration of retentate with operating time.

ating time when its temperature is above its boiling point. Similar to the liquid feed, the dehydration time gets shorter with increasing of the feed temperature. The dehydration time is independent of feed flow rate. However, in the case of liquid feed, the dehydration time decreased with the feed flow rate [Song et al., 1996]. Irrespective of the phase of feed, the increasing of feed temperature shortens the dehydration time.

In Fig. 4 the permeate flux in the vapor feed is compared with that in liquid feed by using the Arrhenius plot. The dark region in this figure means the abrupt change of the slope. The slope, which means the activation energy, is changed near the boiling point (0.00283-0.00286 K⁻¹) and its value in the vapor feed is larger than that in liquid feed.
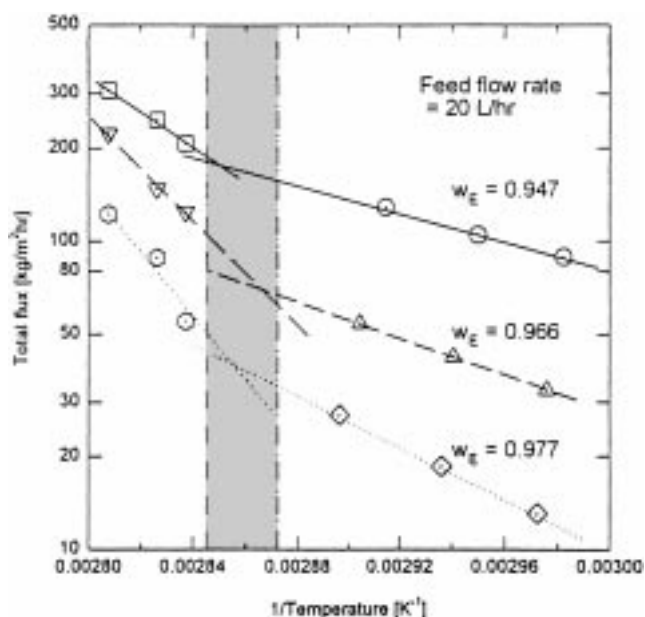

Fig. 4. Arrehenius plot for total flux.

Table 1. The values of P_0 and ΔE in Eq. (11)

Weight fraction of ethanol	P_0 [kg/m²hr]	ΔE [kcal/mol]	State of feed
0.947	9.900×10^5	10.809	Liquid
0.966	3.749×10^7	13.926	Liquid
0.977	4.920×10^{10}	19.359	Liquid
0.947	3.871×10^{15}	26.232	Vapor
0.966	4.724×10^{23}	39.653	Vapor
0.977	3.687×10^{30}	51.269	Vapor

Fig. 5. Selectivity of water in pilot pervaporation.

Fig. 6. Temperature drop of retentate in vapor feeding.

Fig. 7. Temperature drop of retentate by heat loss.

Table 1 shows the values of P_0 and ΔE^v in Eq. (11). The mass transfer for large activation energy is more sensitive to the operating temperature than that for small activation energy. Therefore, the permeation rate in vapor feed has large temperature dependence.
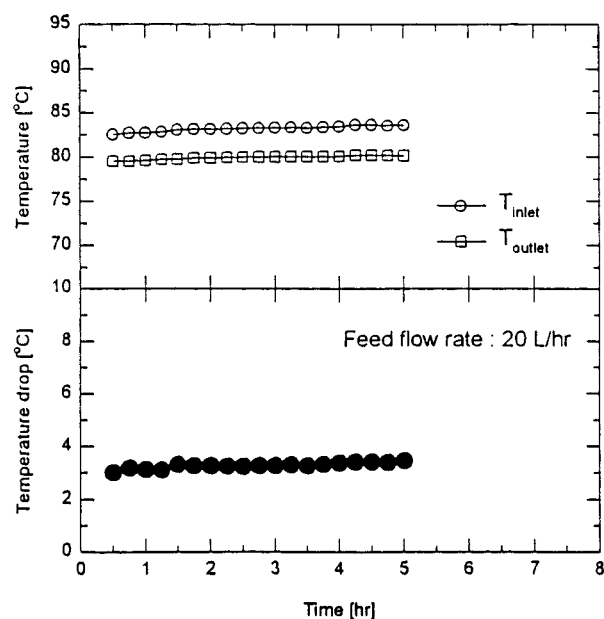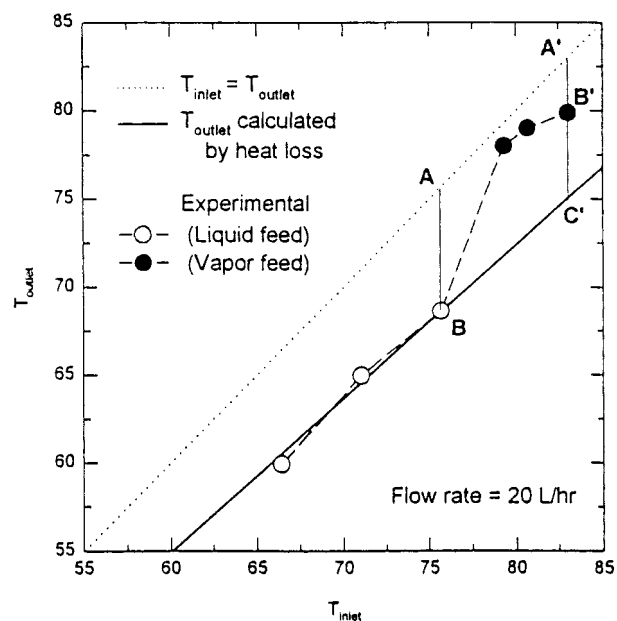
The selectivities for water at various feed concentrations are shown in Fig. 5. It can be found that the selectivities for water increase with the feed concentration. But, the variation of feed flow rate has no influence on the selectivities.

2. Effect of the Feed Temperature

Fig. 6 represents the inlet and outlet temperature of feed with operating time in the case of vapor feed. The temperature drop is small and almost constant with operating time. It is because the energy required for the phase transition of the permeate and the heat loss is supplied with the phase transition of retentate.

The relationship between inlet and outlet temperature at steady-state in the case of liquid and vapor feed is illustrated in Fig. 7. The dotted line means no temperature drop. The temperature drop is about 6 °C for liquid feed, but it is at most about 3 °C for vapor feed. This is mainly due to the retentate phase transition.

The heat loss is proportional to the temperature difference between inside and outside of the membrane module. The temperature drop of the retentate without permeation is only caused by heat loss. Thus, the heat loss can be expressed as follows:

$$Q_{HL} = -a\Delta T_{HL} = -\alpha_o(T_{out} - T_{in}) \tag{12}$$
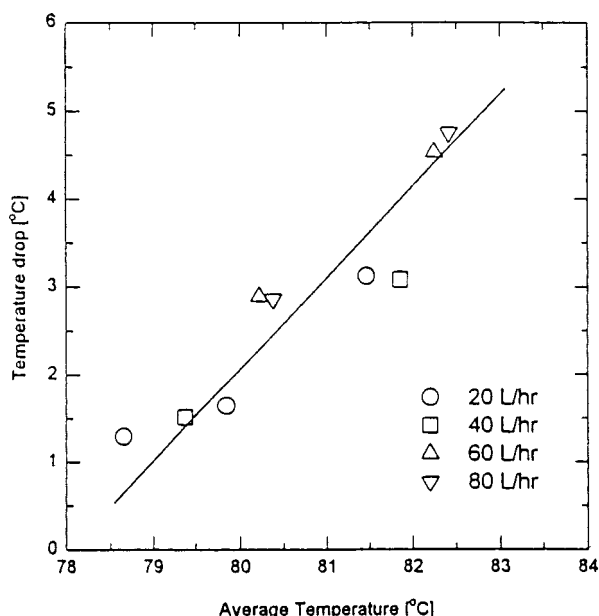
where α_o is the overall heat transfer coefficient and its value is 1.3 kcal/hrK obtained by experiment. Assuming independency of α_o on temperature, the solid line in Fig. 7 is calculated by Eq. (12). The agreement of this line and the experimental data is fairly good. Line AB in this Fig means the temperature drop by the heat loss. If the heat loss could be calculated similarly by Eq. (12) in case of vapor feed, the residual energy as much as the temperature difference (B'C') from the retentate temperature to solid line would be supplied by the retentate phase transition.

3. Effect of the Feed Flow Rate

The value of temperature drop in the case of vapor feed is shown

Table 2. Temperature drop at steady-state in vapor feed operation

Temperature set (°C)	Flow rate (L/hr)	T_{inlet}	T_{outlet}	ΔT
85	20	79.3	78.01	1.29
90	20	80.67	79.03	1.64
	40	80.13	78.62	1.51
	60	81.66	78.77	2.89
	80	81.81	78.95	2.86
95	20	83.02	79.90	3.12
	40	83.76	79.94	3.08
	60	84.51	79.98	4.53
	80	84.79	80.04	4.75

Fig. 8. Temperature drop with average temperature of retentate.

Fig. 9. Effect of total flux on temperature drop.

in Table 2. Increasing of the feed temperature induces the heat loss and then the temperature drop is larger. In the previous contribution [Song et al., 1996], the temperature drop decreases with the feed flow rate in liquid feed. However, in vapor feed, the temperature drop is proportional to the feed flow rate. Fig. 8 represents the temperature drop with the average temperature in membrane module. The z-directional average temperature in the membrane module can be calculated as follows:

$$\overline{T}_z = \frac{\int_0^L T dz}{L} = -\frac{1}{\phi} \frac{FC_p}{A\Delta H_v} \int_{T_{in}}^{T_{out}} \frac{T}{P} dT$$

$$= -\frac{1}{\phi} \frac{FC_p}{A\Delta H_v} \frac{1}{P_o} \int_{T_{in}}^{T_{out}} T \exp\left(\frac{\Delta E}{RT}\right) dT \tag{13}$$

As seen in this equation, the temperature drop increases with the average temperature in module. The increasing of the temperature drop with feed flow rate can be presumed by the variation of the ratio of phase transition. In other words, as the feed flow rate increases, the liquid phase resulting from phase transition influences the vapor phase of the feed and then the temperature drop increases.

Fig. 9 shows the comparison of temperature drop in liquid phase and vapor phase feed. In liquid phase feed, the temperature drop of

retentate is proportional to the flux and is not zero at zero flux. It is mainly due to the heat loss in membrane module itself. However, there is little change of the temperature drop with feed flow rate and low heat loss in vapor feed phase.

CONCLUSION

In the pilot pervaporation experiment, the dehydration time in vapor phase feed was shorter than that in liquid phase feed owing to the part supplementing of evaporation energy of permeate by phase transition of the retentate. Therefore, the temperature drop in this case will be less than in case of liquid phase feed. The variation of temperature drop with permeate flux in vapor phase feed is larger than that in liquid phase due to the heat loss of the membrane module itself. By the control of temperature drop in the pervaporation process the optimum operation temperature would be obtained from this study.

ACKNOWLEDGMENTS

NOMENCLATURE

A : surface area [m²]
C : concentration [kg/m³]
C_p : heat capacity [kcal/kgK]
D : diffusivity [m²/hr]
ΔE : activation energy [kcal/mol]
F : feed flow rate, ΣF_i [L/hr]
ΔH_v : heat of evaporation [kcal/kg]
h : height of channel [m]
J : flux [kg/m²hr]
L : length [m]

Q   : heat flux [kcal/hr]
Q_{HL} : heat loss [kcal/hr]
q   : fraction of phase transition to liquid
P   : permeation rate [kg/m²hr]
R   : gas constant, 1.987 [kcal/molK]
S   : separation factor
T   : temperature [K]
u   : flow velocity [m/hr]
z   : axial distance from the inlet [m]

Greek Letters

α   : heat transfer coefficient [kcal/hrK]
θ   : heat transition ratio defined by Eq. (6)
ρ   : density [kg/m³]
Φ   : heat supply ratio defined by Eq. (7)

Superscripts

b   : bulk phase
d   : downstream side of the membrane
f   : feed
p   : permeate
v   : vapor phase

Subscripts

b   : boiling point
e   : ethanol
ex   : experimental
HL   : heat loss
in   : inside of module
inlet   : inlet
m   : within membrane
max   : maximum
o   : overall
out   : outside of pervaporator
outlet   : outlet
P or p   : permeate
v   : vaporization

y   : vertical direction from membrane surface to downstream

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