

The Separation of Falling Binary Liquid Film in the Presence of Inert Components by Diffusion Distillation

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Abstract. The effects of heat and mass transfer on selectivity and mass fluxes in falling film evaporation of binary mixture on vertical surface, in the presence of inerts in gas (air, helium) and liquid (glycol) phase were investigated. The mathematical model of the process with different simplifying assumptions concerning heat and mass transfer was elaborated. In numerical calculations mass transfer resistances in both gas and liquid phases were considered. Experimental study was performed for 2-propanol-water system in the wide range of concentrations and temperatures. The comparison shows small effect of diffusional cross effects on mass transfer and selectivity.

Keywords: Film Flow, Evaporation, Diffusion Distillation

1. Introduction

The separation of liquid mixtures is of great importance in many industrial processes. Conventional separation methods like distillation, absorption, adsorption are expensive and in many cases detrimental from an ecological point of view. In the studied process of diffusion distillation (King 1971, Fullarton and Schlünder 1986, Palen, Wang, Chen, 2004) the binary liquid mixture is evaporated on the heated tube at the temperature below the boiling point, diffuses through an inert gap and condenses at a lower temperature on the cooled tube. Due to the different diffusivities of individual components through the inerts both in liquid and gas phase the mixture separation effect takes place. The thin falling films flowing down the vertical tubes can be applied as an effective heat and mass transfer mechanism. On account of used thin films (0.05-0.5 mm), experimental results may be useful also in the case of micro flows. Additionally pure diffusion in gas phase and low Re numbers in liquid films are similar to micro scale conditions.

In this work the mathematical model of the process taking into account heat and mass transfer resistances in liquid on evaporation and condensation side and in vapour was elaborated and verified by own experimental data (Ziobrowski and Krupiczka 2007). The present paper aims to study the effect of mixture composition, evaporation temperature and presence of inerts in liquid and gas phase on selectivity and efficiency in diffusion distillation process of binary mixture.

Approximate solutions based on the linearized theory have been presented in literature in a matrix form by Toor (1964), Stewart and Prober (1964), Burghardt and Krupiczka (1979), Krishna (1981), Taylor and Smith (1982). The solution thus obtained are less complex with respect to the fluxes than the exact solution of Maxwell-Stefan equations for multicomponent systems (Krishna and Standart 1976, Krishna and Panchal 1977).

2. Experimental

The main part of the experimental setup, shown schematically in Fig.1., is a wetted wall

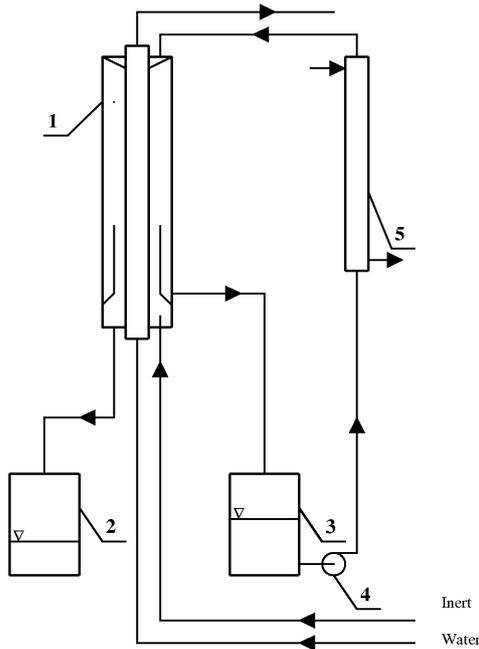


Fig.1. Experimental setup :1-wetted wall column, 2-3 -vessels, 4-pump, 5-heater

column consisting of two concentric tubes (1). The liquid film is introduced on the inside surface of the heated outer tube (26 mm, $l=0.6\text{m}$) and partially evaporated in the annular inert gap. Vapour is condensed on the outside surface of the inner tube (20 mm) cooled with water and collected in a vessel (2). The liquid mixture is gathered in a vessel (3) from which by means of a pump (4) and heater (5) is returned to the wetted wall column (1). The temperature of liquid film is thermostated ($\pm 0.1^\circ\text{C}$). The experiments were performed in isobaric conditions. The temperatures of the falling film, condensate, cooling water were measured by NiCr-Ni thermocouples ($\pm 0.05^\circ\text{C}$ with additional calibration). The flow rates were measured by flow meter and rotameter ($\pm 1.5\%$). The composition of liquid film and condensate were measured with a gas chromatograph Varian Star 3400 ($\pm 2\%$), equipped with J&W DB-5 30 m long column and TCD detector. 2-propanol-water mixture was investigated in the presence of inert in liquid (glycol) and gas (air, helium, argon). The experiments were performed in isobaric conditions for different mixture concentrations, evaporation temperatures and flow rates.

3. Model Equations

The separation of liquid mixtures is performed in an evaporation-condensation process in the presence of inerts in liquid and in gas phase. The schematic diagram of the physical process is shown in Fig. 2. The condensation composition can be determined on the basis of mass and heat balances and the relationship describing vapour-liquid equilibrium. The model equations are formulated on following assumptions:

- the inert gas in the slot is stagnant and isobaric
- mass transfer in the slot is described by a steady-state molecular diffusion in one dimensional coordinate system
- thermodynamic equilibrium is assumed at the liquid-gas interface.

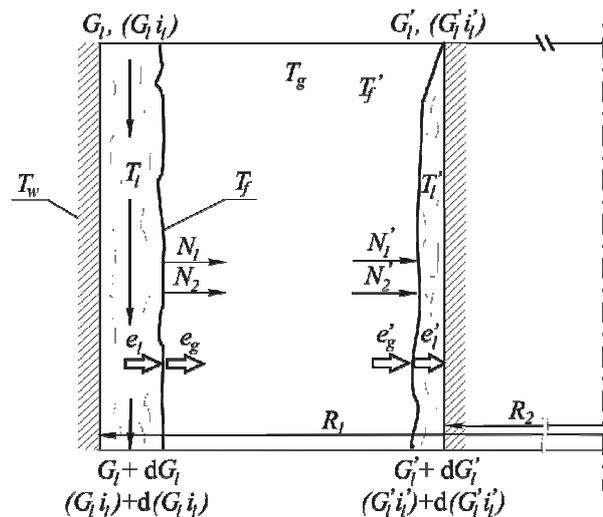


Fig.2. Schematic diagram of the process

With these assumptions the heat balance equations of evaporating liquid film are as follows:

$$G_l \bar{c}_{pl} \frac{dT_l}{dF} = \sum_{j=1}^{n-1} N_j (c_{pl,j} T_f - \bar{c}_{pl} T_l) + h_{l1}(T_w - T_l) - h_{l2}(T_l - T_f) \quad (1)$$

The interface temperatures of evaporating liquids and condensate were calculated from Colburn type equation (Coulson and Richardson 1995) in which heat transfer

through gas layer is treated as conductivity process. The corresponding heat balance equations for evaporating liquid and condensate are as follows:

$$h_{l2}(T_l - T_f) = \frac{2\lambda}{s}(T_f - T_g) + \sum_{j=1}^{n-1} N_j \Delta H_j \quad (2)$$

$$h'_i(T'_f - T'_l) = \frac{2\lambda}{s}(T_g - T'_f) + \sum_{j=1}^{n-1} N'_j \Delta H'_j \quad (3)$$

Mass balance equations for evaporating liquid are:

$$\frac{dG_l}{dF} = -N \quad \frac{dG_{l,j}}{dF} = -N_j \quad j=1 \dots n \quad (4)$$

and corresponding (appropriate) relationships for condensing vapor are taken from:

$$\frac{dG'_i}{dF'} = N' \quad \frac{dG'_{l,j}}{dF'} = N'_j \quad j=1 \dots n \quad (5)$$

According to the layer flow model the interface condensate concentrations at a given cross section were calculated as:

$$x'_j = \frac{N'_j}{N'} \quad j=1 \dots n \quad (6)$$

Vapour composition on the evaporation and condensation side are described by:

$$y_j = \frac{\gamma_j x_j p_j^*(T)}{p} \quad (7)$$

$$y'_j = \frac{\gamma'_j x'_j p_j^*(T')}{p} \quad (8)$$

The activity coefficients γ_j were calculated by the Wilson equation (Gmehling and Onken 1968) and the vapour pressure p_j^* from Antoine equation.

The molar mass fluxes of diffusing species through the inert gap can be determined from the general solution of the Stefan-Maxwell equations, which for n diffusing species and one inert component can be written in the form (Burghardt and Krupiczka 1976, Krishna and Standart 1979, Taylor 1981):

$$\mathbf{N} = h_{Mg}(\mathbf{D}') \frac{\Delta y}{y_{Im}} \quad (9)$$

where $\mathbf{N}^T = (N_1, N_2, N_{n-1})$, $\Delta \mathbf{y}^T = (\Delta y_1, \Delta y_2, \Delta y_{n-1})$ and the elements of reciprocal matrix of diffusion coefficients in the gaseous phase \mathbf{D}^{-1} are given by :

$$D_{k,k}^{-1} = \frac{1}{\bar{y}_l} \sum_{j=1, j \neq k}^n \frac{y_j}{D_{k,j}} = \frac{1}{D_{k,m}} \quad (10)$$

$$D_{k,j}^{-1} = -\frac{\bar{y}_k}{y_l D_{k,j}} \quad (11)$$

and the logarithmic mean concentration of inert component is given as:

$$y_{Im} = \frac{y_l - y_{l,f}}{\ln \frac{y_l}{y_{l,f}}} \quad (12)$$

The similar equations can be obtained for diffusing species through inert component in the liquid phase (glycol) as follows:

$$\mathbf{N} = h_{Ml}(\mathbf{D}') \frac{\Delta x}{x_{Im}} \quad (13)$$

where $\mathbf{N}^T = (N_1, N_2, N_{n-1})$, $\Delta \mathbf{x}^T = (\Delta x_1, \Delta x_2, \Delta x_{n-1})$ and the elements of reciprocal matrix of diffusion coefficients in the liquid phase \mathbf{D}^{-1} are given by :

$$D_{k,k}^{-1} = \frac{1}{\bar{x}_l} \sum_{j=1, j \neq k}^n \frac{y_j}{D_{k,j}} = \frac{1}{D_{k,m}} \quad (14)$$

$$D_{k,j}^{-1} = -\frac{\bar{x}_k}{x_l D_{k,j}} \quad (15)$$

where $x_{l,m}$ is the logarithmic mean concentration of inert component in the liquid phase.

The selectivity of the process is defined by relationship:

$$S = \frac{x'_1}{x_1} \quad (16)$$

In general Model I both diffusional and thermal resistances et. al for evaporating liquid film and condensate film were taken into account (Krupiczka et al., 2000, 2002, 2004, Ziobrowski and Krupiczka 2001). The elements of reciprocal matrix of diffusion coefficients in the gaseous and liquid phases \mathbf{D}^{-1} were calculated according to Eqs.10-11 and 14-15. In Model II only diagonal elements of reciprocal matrices in a gas and liquid phase were taken into account.

In numerical calculation the heat transfer coefficient in the evaporating liquid film was determined from Chun-Seban correlation (h_{l1}) (Chun and Seban 1971) and Modina correlation (h_{l2}) (Modine, Paarith, Toor 1963). On condensation side Nusselt correlation for laminar film was applied (Rohsenov and Hartnett 1973). Mass transfer coefficient in liquid film was calculated from Hobler -

Kędzierski correlation (Hobler and Kędzierski 1983).

To solve the system of differential equations (Eqs. 1, 4, 5). the GERK method proposed by Champine and Watts (Champine and Watts 1976).was used. On each step of integration both interfacial temperatures T_f and T_f' and interface concentrations x_l and x_f' must be calculated by solving the set of four nonlinear equations (Eqs. 2, 3, 9, 13). The calculations were done by using the SOSNLEQ method by H.A. Watts.

3. Experimental results

The comparison of measured total mass fluxes at azeotropic composition of 2-propanol-water mixture for inert in gas phase (air, helium) is presented in Fig.3-4, for inert gaps width 3,5,7 mm and evaporaton temperatures 30-70 °C.

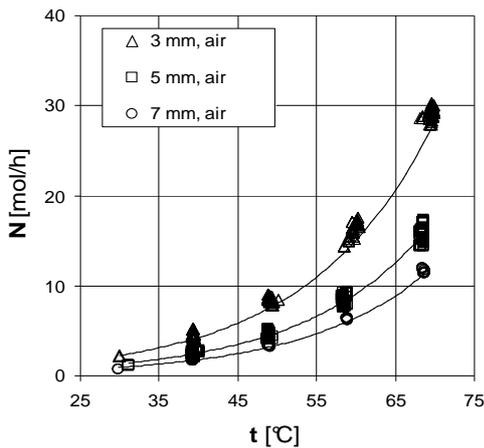


Fig.3. Comparison of measured mass fluxes for air.

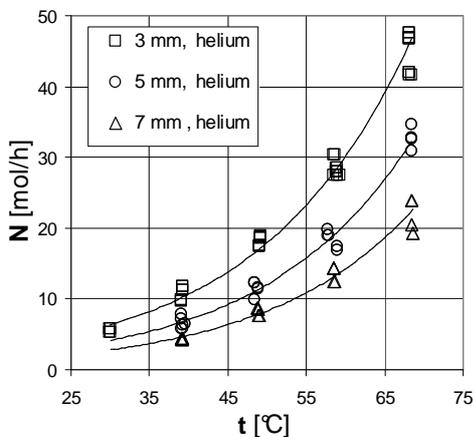


Fig.4. Comparison of measured mass fluxes for helium.

As can be seen the measured mass fluxes rise with evaporation temperature and gap width. For helium as an inert gas measured mass fluxes are almost two times higher than mass fluxes obtained for air. The solid line represent the calculation results according to Model I in the case of absence of inert in liquid phase.

Fig.5 shows the comparison of measured mass fluxes for inert gap width 5mm filled with air and 0, 20, 80% wght of inert in liquid phase (glycol). Measured mass fluxes increase with evaporation temperature and decrease with higher contents of glycol in evaporating mixture. For 80%wght concentration of glycol the decreasing is significant.

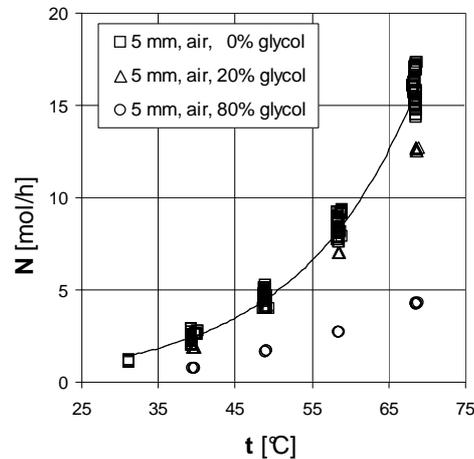


Fig.5. Comparison of measured mass fluxes for inerts in both phases.

If the binary mixture is evaporated below the boiling point in the presence of an inert component the separation effect depends not only on the vapour-liquid equilibrium but also on different diffusivities of two volatile components in inert. In Fig.6 the separation of an azeotropic binary mixture by distillation and by investigated process of diffusion distillation is shown for gap width 3mm and evaporaton temperatures 40-70 °C. In this figure the equilibrium data for 2-propanol-water mixture ($p=1\text{atm}$, solid line) and experiments with inerts in both phases (air, glycol) and only in gas (air) phase are presented. The measured values of concentration of more volatile components in condensate x_1 increase with rising evaporation

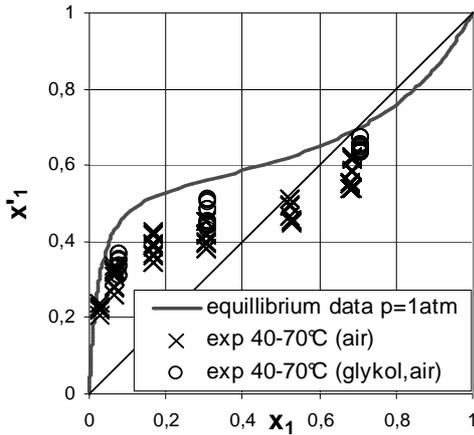


Fig.6. Comparison of equilibrium data with experiments for 2-propanol-water mixture.

temperature. The experimental values in the case of inerts in both phases are slightly higher than those for inert only in gas phase. At the azeotropic point or for the composition above that, the higher volatility of 2-propanol is compensated by the higher diffusivity of water vapour in air. Experimental results show the significant separation effect even in an azeotropic point.

4. Calculation results

In fig.7-8 the experiments and calculations are presented for inert only in gaseous phase.

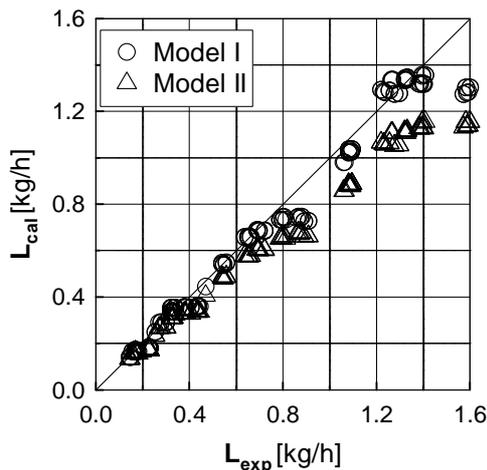


Fig.7. Comparison of calculated and experimental mass fluxes for Model I,II.

The comparison of calculated and measured mass fluxes of 2-propanol-water mixture is presented in Figure 7 both for the case when nondiagonal elements of matrix

D^{-1} in gas phase were taken into account (Model I) and when they were neglected (Model II). For higher values of mass fluxes the calculated values are lower than experimental ones. The differences between both models are rather small except high values of mass fluxes for which Model I predicts higher values than Model II.

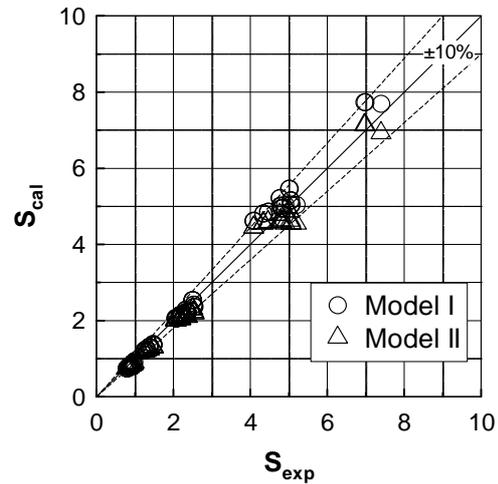


Fig.8. Comparison of calculated and experimental selectivities for Model I,II.

The scattering between the calculated and experimental values of selectivity lies in the range of about $\pm 10\%$ (Fig.8). Best agreement between experiments and calculation results was achieved when heat and mass resistances in both phases were taken into account with all elements of reciprocal matrix of diffusion coefficients in the gaseous phase.

5. Conclusions

Based on Stefan-Maxwell equations and different assumptions concerning mass transfer resistances in both phase two mathematical models of the process of film evaporation and condensation through an inert were elaborated. In both models the heat and mass transfer resistances in liquid films (on evaporation and condensation side) were taken into account. In the simplified model nondiagonal elements of reciprocal matrix of diffusion coefficients in the gaseous and liquid phase were neglected.

The results of numerical calculation for both models give good agreement with experimental data in the case of absence of inert in liquid. Better results were obtained for

Model I in which diffusional cross effects in gas phase were taken into account (Fig.7,8). Selectivity of the process is strongly dependent on 2-propanol concentration at the evaporation side. The calculations based on both models give similar results (Fig.8), what suggests that the influence of diffusional cross effects on selectivity in this case is not significant.

NOMENCLATURE

c_p	–specific heat at const. pressure, J kmol ⁻¹ K ⁻¹
d	–diameter of the tube, m
e, q	–heat flux, kWm ⁻²
F	–heat transfer area, m ²
G	–molar flux, kmol h ⁻¹
h	–heat transfer coefficient, W m ⁻² K ⁻¹
h_M	–mass transfer coefficient, m s ⁻¹
ΔH	–enthalpy of vaporization, J kmol ⁻¹
L	–mass flux, kg h ⁻¹
N	–molar mass flux density, kmol m ⁻² s ⁻¹
p	–pressure, Pa
T	–temperature, K
x	– molar fraction in liquid phase
y	–molar fraction in vapor phase
γ	–activity coefficient
λ	–thermal conductivity W m ⁻¹ K ⁻¹

SUBSCRIPTS

f	–condition at the gas liquid interface
g	–gas
l	–inert
j, k	–refer to component
l	–liquid
m	–logarithmic mean
w	–wall

SUPERSSCRIPTS

'	–refer to condensation side
-	–average value
*	–refer to equilibrium condition

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