

INTEGRATED EVAPORATION-CONDENSATION PROCESS OF BINARY LIQUID MIXTURE SEPARATION

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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 both in gas and liquid phases were considered. Experimental study was performed for 2-ipropanol-water system in the wide range of concentrations and temperatures. The comparison shows small effect of diffusional cross effects on mass transfer and selectivity.

INTRODUCTION

The separation of liquid mixtures is important in many industrial processes connected with chemical, pharmaceutical production, food processing, dehydration of organic mixtures, cooling and evaporation [1-2]. 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 [3-4] 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. 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 [5]. The present paper studies 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 [6], Stewart and Prober [7], Burghardt

and Krupiczka [8], Krishna [9], Taylor and Smith [10]. The solutions thus obtained are less complex with respect to the calculated fluxes than the exact solution of Maxwell-Stefan equations for multicomponent systems (Krishna and Standart [11], Krishna and Panchal [12].

NOMENCLATURE

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

Subscripts

f	interface
g	gas
I	inert
j, k	refer to component
l	liquid
m	logarithmic mean
w	wall

Superscripts

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

EXPERIMENTAL

The main part of the experimental setup, shown schematically in Fig.1., is a wetted wall 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 (16-20 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 ($\Delta T = \pm 0.1^\circ\text{C}$ with additional calibration with high precision Pt100 sensor). The flow rates were measured by flow meter ($\Delta V_f = \pm 0.2 \text{ l/h}$) and rotameter ($\Delta V_r = \pm 5 \text{ l/h}$). The composition of liquid film and condensate were measured with a gas chromatograph Varian Star 3400 ($\Delta x = \pm 0.02$) equipped with J&W DB-5 30 m long column and TCD detector. Condensate flow rate was evaluated by measuring condensate volume (with calibrated cylinder $\Delta V = \pm 0.5 \text{ cm}^3$) and time $\Delta t = \pm 1 \text{ s}$. The error of measuring mass flux density and selectivity were $N = \pm 0.25 \text{ kg}/(\text{m}^2 \text{ h})$ and $S = \pm 0.05$ (total differential error method). 2-propanol-water mixture was investigated in the presence of inert in liquid (glycol) and gas (air, helium, argon). The experiments were performed for different mixture concentrations, evaporation temperatures and flow rates.

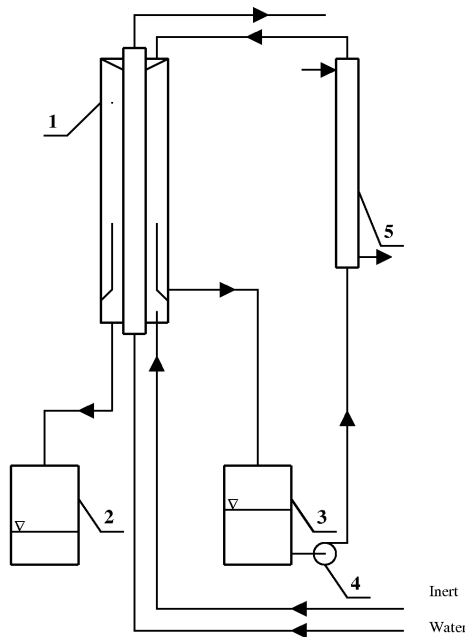


Figure 1 Experimental setup : 1-wetted wall column, 2-3 -vessels, 4-pump, 5-heater

MODELS 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.

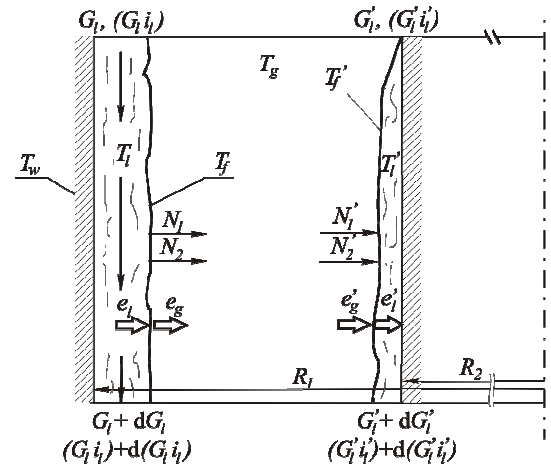


Figure 2 Schematic diagram of the process

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 liquid and condensate were calculated from Colburn type equation [13] 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:

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

$$h_l' (T_f' - T_l') = \frac{2\lambda}{s} (T_g - T_f') + \sum_{j=1}^{n-1} N_j' \Delta H_j' \quad (3)$$

Mass balance equations for evaporating liquid are:

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

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

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

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 [14] 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 [15-17]:

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

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

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

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

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

$$y_{Im} = \frac{y_I - y_{I,f}}{\ln \frac{y_i}{y_{i,f}}} \quad (12)$$

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

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

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

where $x_{I,m}$ 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 for evaporating liquid film and condensate film were taken into account [18-21]. 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_{II}) [22] for turbulent film:

$$Nu = 0,0038 Re^{0,4} Pr^{0,65} \quad (17)$$

verified in our previous experiments [19] and Modina correlation (h_{I2}) [23]. On condensation side Nusselt well known correlation for laminar film was applied [24]:

$$Nu = 1.5 Re^{-0,22} \quad (18)$$

Mass transfer coefficient in liquid film was calculated from Hobler - Kędzierski correlation [25].

To solve the system of differential equations (Eqs. 1, 4, 5), the GERK method proposed by Shampine and Watts [25] was used. On each step of integration both interfacial temperatures T_f and T'_f and interface concentrations x_I 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.

EXPERIMENTAL RESULTS

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

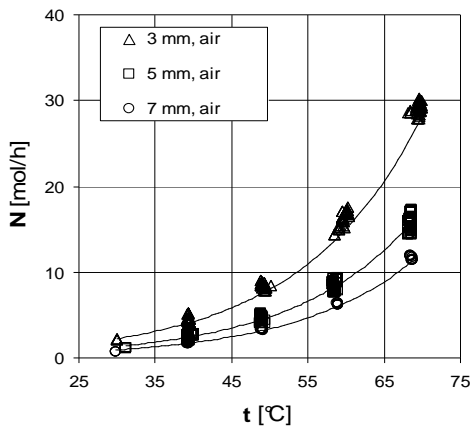


Figure 3 Comparison of measured mass fluxes for air.

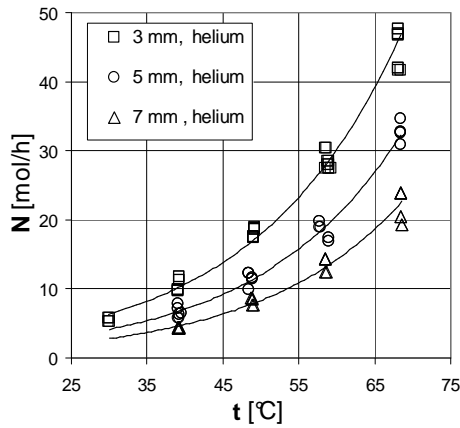


Figure 4 Comparison of measured mass fluxes for helium.

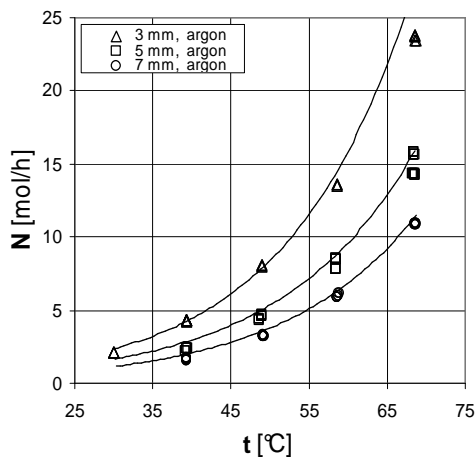


Figure 5 Comparison of measured mass fluxes for argon.

As can be seen the measured mass fluxes rise with evaporation temperature and gap width. For helium as an inert gas the 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.6 shows the comparison of measured mass fluxes for azeotropic concentration of 2propanol-water mixture (inert gap width 5mm filled with air and different mass concentrations of glycol as an inert in liquid phase) in evaporation temperature range of 40-70°C.

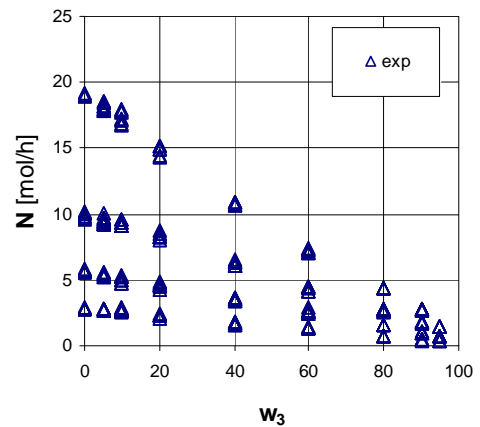


Figure 6 Comparison of measured mass fluxes for inerts in both phases.

Measured mass fluxes increase with evaporation temperature (respectively 40,50,60,70°C) and decrease with higher contents of glycol in evaporating mixture. The decreasing of measured mass fluxes with concentration of glycol is significant.

If the binary mixture is evaporated below the boiling point in the presence of an inerts component the separation effect depends not only on the vapour-liquid equilibrium but also on different diffusivities of two volatile components in inerts. In Fig.7 the separation of an azeotropic binary mixture by investigated process of diffusion distillation is shown for gap width 5mm filled with air as an inert gas and for different concentrations of glycol as an inert in liquid phase. Experiments were performed in evaporation temperature range 40-70 °C. In this figure measured values of selectivity increase with concentration of glycol in liquid phase. For the 90% glycol concentration measured values of selectivity are ten times higher then values obtained without glycol in liquid phase. The effect of evaporation temperature on selectivity is not significant in the range 40-70°C.

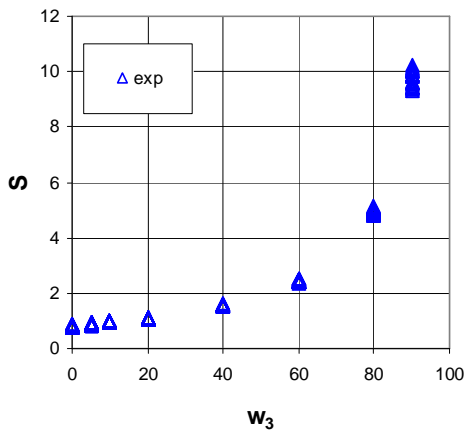


Figure 7 Measured values of selectivity for inerts in both phases

At the azeotropic point and for the composition above that, the higher volatility of 2-propanol is compensated by the higher diffusivity of water vapour in air so the mixture can be separated by diffusion distillation.

CALCULATION RESULTS

In fig.8-9 the experiments and calculations are presented for inert only in gaseous phase.

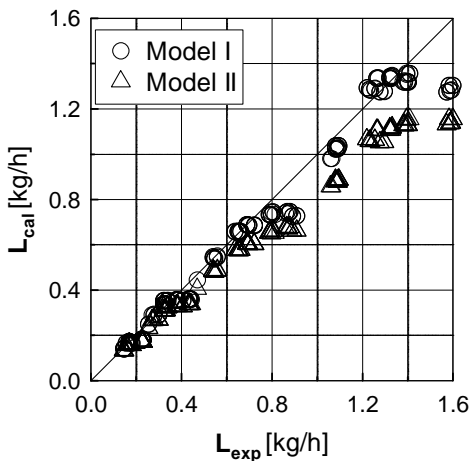


Figure 8 Comparison of calculated and experimental mass fluxes for Model I,II

The comparison of calculated and measured mass fluxes of 2-propanol-water mixture is presented in Figure 8 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.

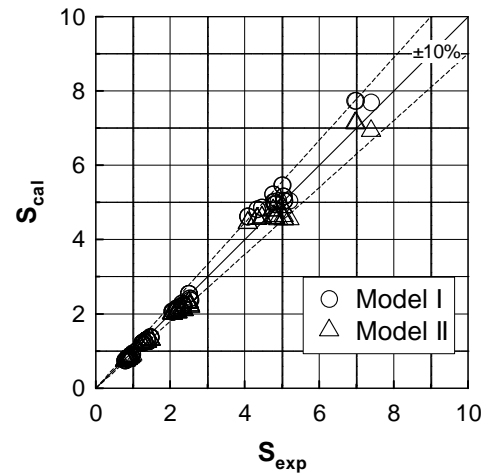


Figure 9 Comparison of calculated and experimental selectivities for Model I,II.

The scattering between the calculated and experimental values of selectivity lies in the range of about $\pm 10\%$ (Fig.9).

The 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. The errors between experimental and calculated values for both models are presented in Table 1.

Tab. 1

Model	Average error	Standard deviation	r^2
Model II	0.0592	0.0810	0.9818
Model I	0.0317	0.0463	0.9987

CONCLUSION

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.8,9).

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.9), what suggests

that the influence of diffusional cross effects on selectivity in this case is not significant.

REFERENCES

- [1] King, C.J., 1971, Separation Processes, Mc Graw-Hill Book Company, N.Y.
- [2] Van Hof, V., Van den Abeele L., Buekenhoudt A., Dotremont C., Leysen R., 2004, Economic comparison between azeotropic distillation and different hybrid systems combining distillation with pervaporation for the dehydration of izopropanol, *Separ. Purif. Tech.*, 37, 33.
- [3] Fullarton, D. and Schlünder, E.U., 1986, Diffusion distillation-a new separation process for azeotropic mixtures Part I: Selectivity and Transfer Efficiency, *Chem. Eng. Proc.*, 20, 255.
- [4] Palen, J.W., Wang, Q.I., Chen, J.C., 2004, Falling film evaporation of binary mixtures, *AIChE Journal*, vol. 40, 207.
- [5] Ziobrowski, Z. and Krupiczka, R., 2007, Separation of liquid mixtures by diffusion distillation, *Chem. Eng. Proc.*, 28, 413.
- [6] Toor, H.L., 1964, Solution of the linearized equations of multicomponent mass transfer, *AIChE J.*, 10, 448.
- [7] Stewart, W.E. and Prober, R., 1964, Matrix calculation of multicomponent mass transfer in isothermal systems, *Ind. Enging. Chem. Fundam.*, 3, 324.
- [8] Burghardt, A. and Krupiczka, R., 1979, *Convective mass transfer in multicomponent systems analysis and relationships defining mass transfer coefficients*, *Inż. Chem.*, 5, 487.
- [9] Krishna, R., 1981, Ternary mass transfer in a wetted wall column – significance of diffusional interactions. I-Stefan diffusion, *Trans. Inst. Chem. Engng*, 59, 35.
- [10] Taylor, R. and Smith, L.W., 1982, On some explicit approximate solutions of the Maxwell – Stefan equations for the multicomponent film model, *Chem. Engng. Commun.*, 14, 361.
- [11] Krishna, R. and Standart, G.L., 1976, A multicomponent film model incorporating an exact matrix method of solution to Stefan-Maxwell equations, *AIChE J.*, 22,383.
- [12] Krishna, R. and Panchal C.B., 1977, Condensation of binary mixtures in the presence of an inert gas, *Chem. Engng. Sci.*, 32,741.
- [13] Coulson, J.M. and Richardson, J.F., 1995, *Chemical Engineering, Fluid Flow, Heat Transfer and Mass Transfer*, V.1, Butterworth Heinemann.
- [14] Gmehling, J. and Onken, U., 1968, Vapour-liquid equilibrium at normal pressure, Pregamon Press.
- [15] Burghardt, A. and Krupiczka, R., 1976, *Międzyfazowy transport masy w układach wieloskładnikowych*, *Inż. Chem.*, VI, 1, 23.
- [16] Krishna, R. and Standart, G.L., 1979, Mass and energy transfer in multicomponent system, *Chem. Engng. Commun.*, 3, 201.
- [17] Taylor, R., 1981, On exact solution of the Maxwell-Stefan equations for the multicomponent film model, *Chem. Eng. Commun.*, 10, 61.
- [18] Krupiczka, R., Rotkegel, A., Ziobrowski, Z., 2000 The influence of mass transport on the heat transfer coefficients during the boiling of multicomponent mixtures, *Int. J. Therm. Sci.*, 39, 667.
- [19] Krupiczka, R., Rotkegel, A., Ziobrowski, Z., 2002, Heat transfer to evaporating liquid films within a vertical tube, *Chem. Eng. Proc.*, 41,89.
- [20] Krupiczka, R., Rotkegel, A., Ziobrowski, Z., 2004 A simplified method of calculation of the heat transfer coefficients during boiling of multicomponent mixtures, *Inż. Chem. Proc.*, 25, 189.
- [21] Ziobrowski, Z. and Krupiczka, R., 2001, Wpływ ruchu masy na wymianę ciepła przy grawitacyjnym filmowym spływie cieczy dwuskładnikowej *Inż. Chem. Proc.*, 22, 3E, 1561.
- [22] Chun, K.R. and Seban R.A., 1971, *J. Heat Transfer Trans ASME*, 391.
- [23] Modine A.D., Paarish E.B., Toor H.L., 1963, *AIChE J.*, 3, 348.
- [24] Rohsenov W.M. and Hartnett I.P., 1973, *Handbook of Heat Transfer*, NY, McGraw-Hill. [5] Feddauti, M., Meftah H., Mir A., 2006, *Numerical computation of the evaporative cooling of falling water film in turbulent mixed convection inside a vertical tube*, *Heat and Mass Transfer*, 33, 917.
- [25] Hobler T. and Kędzierski S., 1983, *Chem. Stos.*, 18,3.
- [26] Shampine L.F. and Watts H.A., 1976, *ACM Trans. on Math. Software (TOMS)*, v.2 n.2, 172.