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THE SIMULATION OF STEADY STATE BEHAVIOUR OF THE DEPHLEGMATION OF MULTI-COMPONENT MIXED VAPOURS

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Abstract – The partial condensation or dephlegmation process is generally used for the production of liquid reflux and vaporous distillate with an additional fractionation in wetted wall column heat exchangers. All known calculations of the performance of vapour condensers are based on a film model, originally derived for binary vapour systems by Ackermann and by Colburn and Drew and generalized for multi-component vapour systems by Standart and Krishna using a general matrix models for the multi-component mass transfer with the more accurate model of Standart and Krishna is given for the partial condensation of a ternary vapour system.

NOMENCLATURE

A,	interfacial surface [m^2];
a,	interfacial surface per height [m];
c,	molar density [kmol m^{-3}];
Cp,	molar heat capacity [J kmol^{-1} °C^{-1}];
d,	tube diameter [m];
$\dot{E}$,	flux of enthalpy [J h^{-1}];
$\dot{e}$,	rate of enthalpy [J h^{-1} m^{-2}];
F,	cross-section [m^2];
f,	function;
g,	acceleration due to gravity [m h^{-2}];
h,	specific molar enthalpy [J kmol^{-1}];
$\mathscr{H}$,	heat transfer coefficient (total) [J h^{-1} m^{-2} °C^{-1}];
$[J]$,	matrix of unity;
l, L,	tube length [m];
Δl,	length of tube element [m];
M,	average molar weight [kg kmol^{-1}];
$\dot{M}$,	mass flux [kg h^{-1}];
N,	mole number per height [kmol];
$\dot{N}$,	mole flux of the more volatile component (A) [kmol h^{-1}];
$\dot{n}$,	mole rate of the more volatile component (A) [kmol h^{-1} m^{-2}];
r,	inner tube radius [m];
T,	temperature [°C];
t,	time [h];
y,	concentration [kmol kmol^{-1}];
u,	velocity [m h^{-1}];
Re,	Reynolds number $= u\, d\rho/\eta$;
Pr,	Prandtl number $= Cp\eta/\lambda$;
Sc,	Schmidt number $= \eta/\rho D$.

Greek symbols

α,	heat transfer coefficient [J h^{-1} m^{-2} °C^{-1}];
β,	mass transfer coefficient [kmol h^{-1} m^{-2}];
δ,	thickness of film [m];
λ,	thermal conductivity [J h^{-1} m^{-1} °C^{-1}];
ρ,	density [kg m^{-3}];
η,	viscosity [kg m^{-1} h^{-1}];
$[\beta]$,	matrix of the zero flux mass transfer coefficients of the binary pairs;
$[\beta]$,	matrix of the non zero flux mass transfer coefficients of the binary pairs;
$[\Phi]$,	matrix defined by equation (1a, b);
$[\Theta]$,	matrix of the generalized Ackerman/Colburn-Drew Correction factors.

Subscripts

i, j, k,	index of the component;
b,	bulk;
d,	vapour;
f,	liquid;
g,	interface;
k,	coolant;
m,	maximum;
o,	top of the tube;
u,	bottom of the tube;
w,	wall;
○	char. Ackermann–Colburn–Drew correction factors.
●	

INTRODUCTION

THE BASIC physical phenomena of the partial condensation illustrated for binary vapour systems are outlined by Blaß [1], Stephan [2], etc. Kirschbaum [3] defined the partial condensation as a unidirectional vapour–liquid mass transfer. As opposed to this, Hausen and Schlatterer [4] found that the partial condensation is a non-adiabatic rectification without reflux at the top of the column, i.e. a mutual mass

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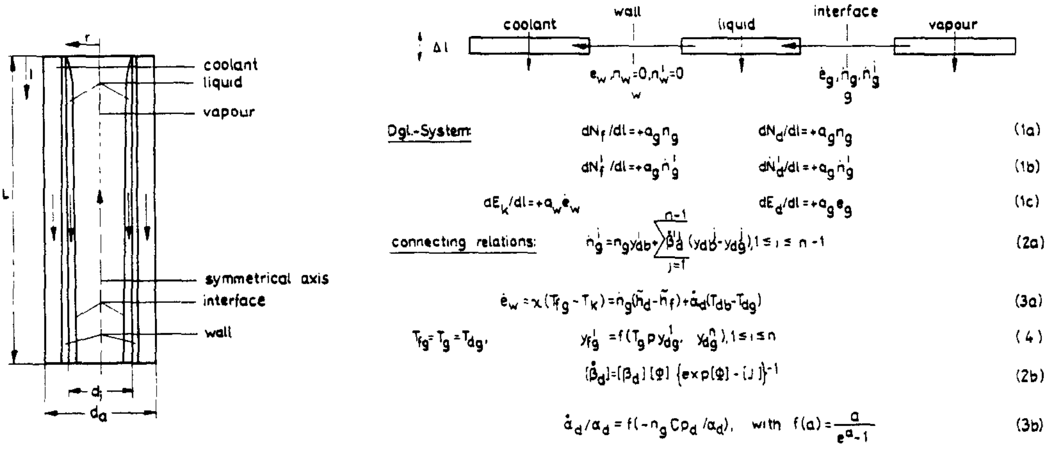
transfer by rectification superposed by condensation. As shown by Begemann [5] in experiments, the results obtained by partial condensation including mutual mass transfer are better than those obtained by partial condensation as defined by Kirschbaum.

A general model of the simultaneous heat and mass transfer during the rectification of binary vapour systems is based on the extended film theory, which was first expounded by Colburn and Drew [6]. This model has been used by many authors for the design of condensers for binary vapour mixtures [4–9] and for the design of condensers for one or more of the vapours of a vapour–gas system [10–13]. The Ackermann–Colburn–Drew equations were extended to mixed vapours with more than two components by Toor [14] and Stewart and Prober [15]. A corrected version of the multi-component film model incorporating a generalized matrix method for the solution of the Stefan–Maxwell equations was presented by Krishna and Standart [16] and Krishna *et al.* [17]. This model only represents the typical transport characteristics of the multi-component mass transfer systems with diffusional interaction, such as osmotic diffusion, diffusion barrier and reverse diffusion, which are discussed in detail by Toor [14] and which are not possible for simple two-component systems. This model was used by Krishna *et al.* [17] for the condensation of a five-component hydrocarbon vapour mixture accompanied by hydrogen as the inert gas component, flowing down inside a vertical tube heat exchanger in co-current to its condensate. For a negligible liquid-side mass transfer resistance, Kirschbaum assumes that the interface concentration of the condensing vapour molar rate is equal to its liquid-side equilibrium concentration and this is in opposition to the assumption of Colburn and Drew, Hausen and Schlatterer, etc. In this paper Krishna and Standart compared three most well-known mass transfer models and demonstrated that the deviations of the separation calculated for these simpler models related to the matrix model are over 20%, if the condensation of a multi-component vapour in the presence of inert gases is chosen as the simulated mass transfer operation. In [18] Bandrowski and Kubaczka published new simulation results of the same mass transfer operation, comparing the models of Toor [14], Stewart and Prober [15], Krishna and Standart [17], Burghardt and Krupiczka [19] and Schrodt [13] with experimental results obtained by Mizushina *et al.* [22] and Porter and Jeffreys [21]. Summarizing these papers, it is found that the first three models are of roughly equal quality, that the matrix model of Krishna and Standart gives the most precise description of multi-component mass transfer but also requires the most computing time, and that the differences of separation calculated by these three models are of little significance.

In this paper the Standart–Krishna general matrix film method is used for the ternary vapour dephlegmation in a vertical tube condenser with a vapour stream flowing upwards in counter-current to the condensate flow and to the coolant in the tube annular section (see Fig. 1). For the dephlegmation of a ternary vapour with negligible mass transfer resistance, the Colburn–Drew conditions are applied, namely that the concentration of the condensing vapour molar rate is lower than the liquid-side equilibrium concentration at the interface of the same component.

THE MACROSCOPIC MODEL OF THE DEPHLEGMATION

The balances of coupled momentum, heat and mass transfer of vapour, liquid and coolant can be derived by integration of the microscopic laws of conservation over the characteristic flow cross-sections. The complete set of differential equations and the set of algebraic equations at the interfaces of the sub-systems are given in Fig. 1. These interface equations are based on the conditions that the rates are uniform and that thermal, material and mechanical equilibria prevail. In connection with initial conditions for l = 0, the set of differential and implicit algebraic equations describes the problem unambiguously.



$$dN_f/dl = +a_g n_g \qquad dN_d/dl = +a_g n_g \tag{1a}$$

$$dN_f^i/dl = +a_g \dot n_g^i \qquad dN_d^i/dl = +a_g \dot n_g^i \tag{1b}$$

$$dE_K/dl = +a_w \dot e_w \qquad dE_d/dl = +a_g e_g \tag{1c}$$

$$\dot n_g^i = n_g y_{db}^i + \sum_{j=1}^{n-1} \dot\beta_d^{ij} (y_{db}^j - y_{dg}^j), 1 \le i \le n-1 \tag{2a}$$

$$\dot e_w = \varkappa (T_{fg} - T_K) = \dot n_g (\tilde h_d - \tilde h_f) + \dot\alpha_d (T_{db} - T_{dg}) \tag{3a}$$

$$T_{fg} = T_g = T_{dg}, \qquad y_{fg}^i = f(T_g p y_{dg}^1, \ y_{dg}^n), 1 \le i \le n \tag{4}$$

$$[\dot\beta_d] = [\beta_d][\Phi]\{\exp[\Phi] - [I]\}^{-1} \tag{2b}$$

$$\dot\alpha_d/\alpha_d = f(-n_g Cp_d/\alpha_d), \quad \text{with } f(a) = \frac{a}{e^a - 1} \tag{3b}$$

FIG. 1. Diagram of apparatus and macroscopic model for multicomponent dephlegmation.

In the case of negligible liquid-side mass transfer resistance, the balances of the mass transfer rate at the interface are reduced to

$$\dot{n}_g^i = \dot{n}_g y_{db}^i + \sum_{j=1}^{n-1} \dot{\beta}_d^{ij}(y_{db}^j - y_{dg}^j), \quad 1 \le i \le n-1. \quad \text{(1a)}$$

The elements of the matrix of zero flux mass transfer coefficients are calculated from the equation

$$[\beta_d] = [B_d]^{-1},$$

where the elements of $[B_d]$ are obtained from

$$B_d^{ii} = y_{db}^i/\beta_d^{in} + \sum_{j=1}^{n} y_{db}^j/\beta_d^{ij}, \quad 1 \le i \le n-1,$$

$$B_d^{ij} = -y_{db}^i(1/\beta_d^{ij} - 1/\beta_d^{in}, \quad 1 \le \mathrm{i}, j \le n-1, i \ne j.$$

The zero flux mass transfer coefficients of the binary pairs β^{ij} can be estimated from standard binary mass transfer correlations using binary diffusion coefficients D^{ij}. From the knowledge of the mass transfer rates $\dot{n}_g^i$, one can obtain the matrix of the non-zero flux mass transfer coefficients using the equation

$$[\dot{\beta}_d] = [\beta_d][\Phi](\exp[\Phi] - [I])^{-1} = [\beta_d][\Theta], \quad \text{(1b)}$$

where the elements of $[\Phi]$ are obtained as

$$\Phi^{ii} = \dot{n}_g^i/\beta_d^{in} + \sum_{j=1}^{n} n_g^j/\beta_d^{ij}, \; 1 \le i \le n-1,$$

$$\Phi^{ij} = -\dot{n}_g^i(1/\beta^{ij} - 1/\beta^{in}), \; 1 \le i, \quad j \le n-1, \quad i \ne j.$$

If liquid subcooling is disregarded, the enthalpy rate relationship between vapour bulk, interface, liquid bulk, wall and coolant bulk is

$$e_w = \mathscr{H}(T_{fg} - T_k) = \dot{n}_g(\tilde{h}_d - \tilde{h}_f) + \dot{\alpha}_d(T_{db} - T_{dg}), \quad \text{(2)}$$

where

$$\dot{\alpha}_d/\alpha_d = f(-\dot{n}_g Cp/\alpha_d), \quad f(a) = \frac{a}{\exp(a) - 1}$$

and

$$\dot{n}_g \tilde{h} = \sum_{i=1}^{n} \dot{n}_g^i h^i,$$

with the coefficient $\mathscr{H}$ accounting for the heat transfer resistances of liquid, wall and coolant. As a result of this simplification, the balances of the liquid-side heat and mass transfer are not required. To approximate the liquid-side momentum transfer, the simplifications of the Nusselt condensation are used. As regards the vapour side, the coefficients of the empirical vapour-side transport laws are calculated according to the analogy of Chilton and Colburn

$$\frac{\beta_d A}{\dot{N}_d} Sc_d^{2/3} = \frac{\alpha_d A}{\dot{N}_d Cp_d} Pr_d^{2/3} = 0.023\, Re_d^{-0.17}. \quad \text{(3)}$$

EXAMPLE AND DISCUSSION

The mathematical macroscopic model described above is used for calculating the dephlegmation of the ternary vapour mixture of methanol, ethanol and water, with the following tube dimensions and operating conditions:

$y_{do} = 0.9420\,\mathrm{kmol\,kmol^{-1}}$;
$\dot{N}_{do} = 0.10\,\mathrm{kmol\,h^{-1}}$;
$\dot{M}_k = 1000\,\mathrm{kg\,h^{-1}}$;
$T_{ko} = 60.00\,°\mathrm{C}$;
$L = 2.50\,\mathrm{m}$;
$d = 0.005\,\mathrm{m}$ (coolant : water).

The Uhde thermophysical properties program package is used to calculate the thermophysical properties.

In order to solve the system of coupled differential and algebraic equations of the heat and mass transfer balances, the boundary value problem caused by the liquid and vapour phases being in counter-current is simplified to an equivalent initial value problem, where the flux, temperature and concentrations of the multi-component vapour at the top of the exchanger are given. The vapour inlet values are then a unique function of the chosen heat and mass transfer relationships and the tube length.

In the first example, the vapour inlet concentrations and flux, and the necessary tube length are given as a function of the chosen enrichment of the first component, methanol, from 77.7 mol% to 94.2 mol% and different vapour outlet concentrations of the third component y_{dbo}^3 [see Fig. 2(a)]. The results show a non-linear relationship of decreasing tube length l and vapour inlet concentration y_{dbu}^2 of ethanol and increasing vapour inlet concentration y_{dbu}^3 of water and the total molar vapour inlet flux with increasing outlet concentration y_{dbo}^3 of water. Figure 2(b) demonstrates the relative percentage deviation of the vapour inlet concentrations, at which the mass transfer is calculated in case I using the multi-component model of Krishna and Standart, in case II the linearized model of Toor and Stewart and Prober, in case III the model of the effective diffusion coefficient of $n - 1$ stagnant components and in case IV the model of the effective diffusion coefficient of non-stagnant components. The deviations of cases II and III in relation to case I are less than -10%, excluding concentrations with low values (see Table 1). For $y_{dbo}^3 \to 0$ or $y_{dbo}^3 \to 0058$, i.e. the binary systems methanol–ethanol or methanol–water, the deviations of the calculated separation of models III and IV related to model I become zero, because all three models are identical for binary systems, and model II does not apply.

In the second example, the vapour inlet concentrations are calculated for a given tube length and vapour outlet conditions using the four models for mass transfer described above. The deviation of the calculated inlet conditions of cases II and III related to

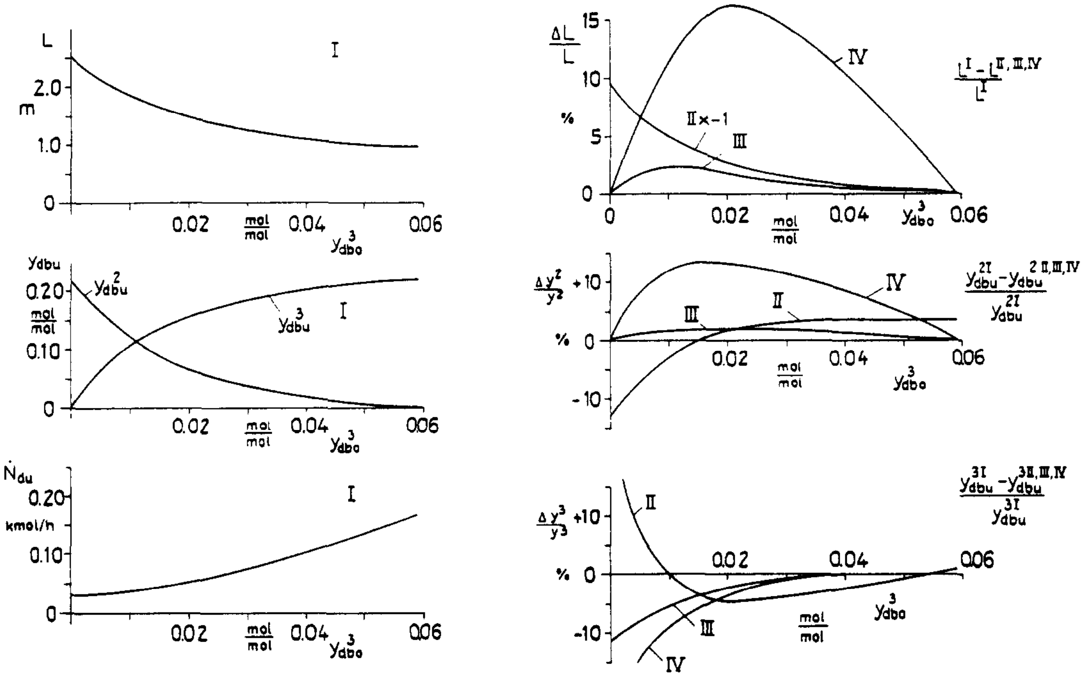


FIG. 2. Tube length, vapour inlet concentration y^2_{dbu} and y^3_{dbu} and molar flux $\dot{N}_{du}$ as a function of vapour outlet concentration y^3_{dbo}.

Table 1. Comparison of the four mass transfer models for the same vapour outlet bulk concentration of the third component (y^3_{dbo} = 0.03)

Case	Length (m)	Molar flux liquid (kmol h^{-1})	vapour	Vapour inlet bulk concentration y^1_{dbu} (kmol kmol^{-1})	y^2_{dbu}	y^3_{dbu}
I	1.56	0.0249	0.0320	0.7772	0.0652	0.1577
II	1.54	0.0249	0.0320	0.7772	0.0666	0.1563
III	1.59	0.0252	0.0322	0.7772	0.0660	0.1567
IV	1.83	0.0273	0.0343	0.7772	0.0761	0.1469

Table 2. Comparison of the four mass transfer models for the same vapour outlet bulk concentration of the third component (y^3_{dbo} = 0.03)

Case	Length (m)	Molar flux liquid (kmol h^{-1})	vapour	Vapour inlet bulk concentration y^1_{dbu} (kmol kmol^{-1})	y^2_{dbu}	y^3_{dbu}
I	2.51	0.0498	0.0569	0.3978	0.0397	0.5625
II	2.51	0.0512	0.0583	0.3877	0.0442	0.5681
III	2.51	0.0480	0.0551	0.4222	0.0441	0.5337
IV	2.51	0.0388	0.0458	0.5960	0.0771	0.3270

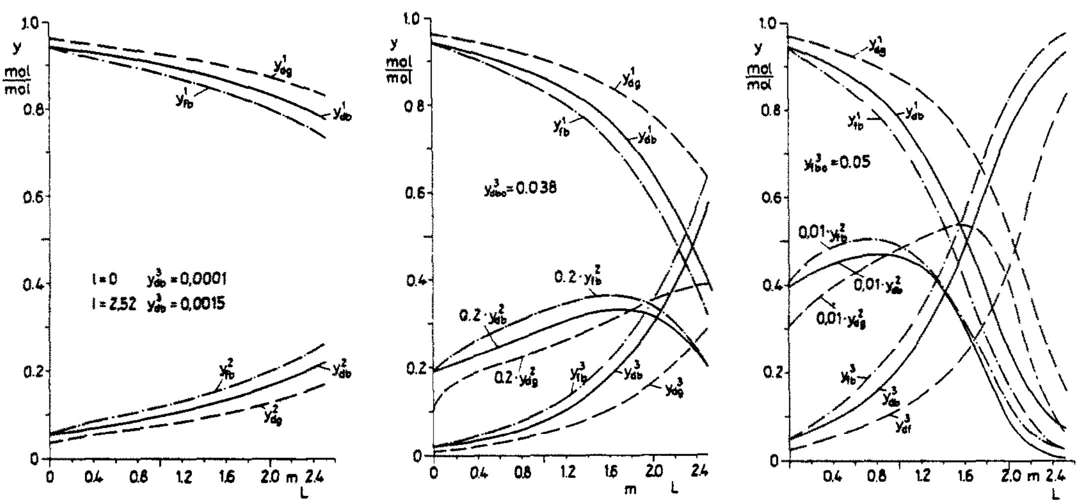


FIG. 3. Vapour bulk concentration profiles as a function of tube length and vapour outlet concentration of the third component.

case I are less than 10%, excluding very low values (see Table 2).

Figure 3(a, b and c) demonstrates the calculated local profiles of the bulk concentration of both phases and the vapour-side interface concentration for different top conditions of the vapour. If the vapour outlet concentration of the third component, water, is raised slightly, fractionation of methanol up to 94 mol% is possible for a vapour with high water concentration. In this case, a characteristic circulation of the medium-volatile component, ethanol, with a significant maximum in the concentration profile, a local equilibrium and a nearly total local evaporation is obtained.

Figure 4 presents the non-zero mass flux mass transfer coefficient $\dot{\beta}_{11}$, $\dot{\beta}_{12}$, $\dot{\beta}_{21}$ and $\dot{\beta}_{22}$ and the total condensation rate $\dot{n}_g$ as a function of the tube length. At the top of the tube, where a nearly total condensation exists, the condensation rate decreases very slightly and increases again gradually with increasing tube length. While the main diagonal elements of the mass transfer matrix increase in a nearly linear manner, the interaction elements $\dot{\beta}_{12}$ and $\dot{\beta}_{21}$ pass through a maximum, they become zero for higher condensation rates at the top and the bottom of the tube. The diagram shows that the interaction effects are not negligible in relation to the main effects, although the deviation with respect to the simpler models are less than 10%.

In Fig. 5 the separation by dephlegmation is presented as a function of the values of the diffusion coefficient for the same upper boundary conditions. In cases with similarly high diffusion coefficients of the first and second component in relation to the third is given in the ternary system, methanol–ethanol–water, high mass transfer rates of the third component are possible. In the given example, the condensation rate of the less volatile component, water, will thus increase with decreasing diffusing resistances of this component in relation to the other two components.

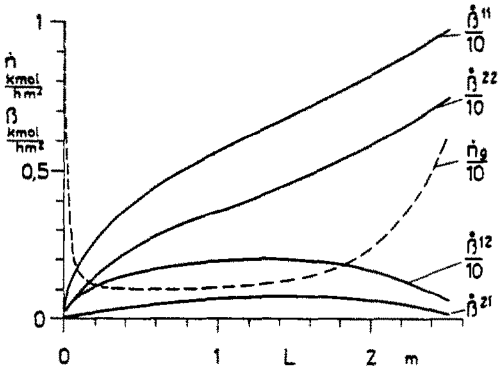


FIG. 4. Non-zero-flux mass transfer coefficients $\dot{\beta}^{ij}$ and condensation rate $\dot{n}_g$ as a function of the tube length.

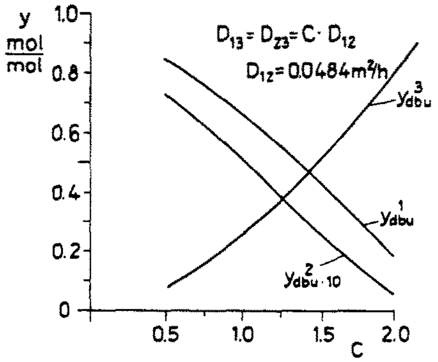


FIG. 5. Vapour inlet bulk concentrations as a function of the diffusion coefficients (l = 2.51 m, y^3_{dbo} = 0.03).

SUMMARY

A general macroscopic model to describe the steady state phenomena of the non-adiabatic rectification and dephlegmation of multi-component vapour systems is presented using the new matrix model for multicomponent mass transfer of Krishna and Standart. Results of computer simulations of this and other simpler known multi-component mass transfer models are given. The results presented demonstrate that the differences in the calculated separation rate with respect to practical condenser design are insignificant as long as the mass transfer rate at the liquid vapour interphase, are high and no additional mass transfer resistances caused by non-transferable components such as inert gases and non-volatile compounds exist.

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SIMULATION DE LA CONDENSATION PARTIELLE STATIONNAIRE D'UN MELANGE DE VAPEURS

Résumé — La condensation partielle est généralement utilisée dans l'obtention du reflux liquide et du distillat de vapeur, avec un fractionnement additionnel dans les échangeurs de chaleur à paroi mouillée. Tous les calculs de performance des condenseurs de vapeur sont basés sur le modèle du film, dérivé pour les systèmes binaires de vapeurs par Ackermann et par Colburn–Drew et généralisé par des systèmes à plusieurs composants par Standart–Krishna en utilisant une méthode matricielle. On donne ici une comparaison des différents modèles approchés et du modèle plus précis de Standart–Krishna, pour la condensation partielle d'un système ternaire de vapeurs.

DIE SIMULATION DES STATIONÄREN DEPHLEGMATIONSVORGANGS VON MEHRKOMPONENTEN-DAMPFGEMISCHEN

Zusammenfassung—Der partielle Kondensations- oder Dephlegmationsprozeß wird allgemein zur Erzielung flüssigen Rücklaufs und dampfförmigen Destillats mit einer zusätzlichen Fraktionierung in Säulenwärmeaustauschern mit benetzter Wand durchgeführt. Alle bekannten Berechnungsmethoden von Dampfkondensatoren basieren auf einem Filmmodell, das ursprünglich von Ackermann und Colburn–Drew für binäre Systeme abgeleitet und von Standart–Krishna für Mehrkomponentensysteme unter Verwendung einer Matrizenmethode verallgemeinert wurde. In dieser Arbeit wird ein Vergleich verschiedener Näherungsmodelle für den Mehrkomponenten-Stoffübergang mit dem genaueren Modell von Standart–Krishna angestellt, und zwar für die partielle Kondensation eines ternären Dampfgemisches.

МОДЕЛИРОВАНИЕ СТАЦИОНАРНОГО РЕЖИМА ДЕФЛЕГМАЦИИ МНОГОКОМПОНЕНТНЫХ СМЕСЕЙ ПАРОВ

Аннотация — Парциальная конденсация, или дефлегмация, обычно используется для получения жидкого конденсата и парового дистиллята при дополнительном фракционировании в колоннах теплообменников со смачиваемыми стенками. Все известные расчёты рабочих характеристик конденсаторов пара основываются на плёночной модели, первоначально разработанной для бинарных паровых систем Акерманном и Колберном–Дрю и обобщенной Стандартом и Кришной на случай многокомпонентных паровых систем с помощью общего матричного метода. В настоящей работе проводится сравнение различных приближенных моделей многокомпонентного массопереноса с более точной моделью Стандарта–Кришны для парциальной конденсации трёхкомпонентной паровой системы.