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MODELLING OF THE SUBSTANCE TRANSFER IN THE GAS-LIQUID SYSTEM WITH CHEMICAL REACTION

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Abstract

In this paper substance transfer phenomena in the multistage reactive system were investigated. Substance transfer between liquid and gas phases in a distillation packed column with reaction esterification was examined. Efficiency of substance transfer were examined by HTU-Height of transfer units and volumetric substance transfer coefficients. The esterification reaction of the ethanol and acetic acid was examined. Based on derived mathematical model the total height of transfer units and individual height of transfer units for the liquid and gas phases were determined. The investigation was performed by computer simulation and experiments. Several correlation models for HTU/NTU and substance transfer coefficients were studied. The correlations for component transfer were derived in quaternary systems ethanol-ethyl acetate-acetic acid -water.

Keywords: Height of transfer units; substance transfer coefficient; multistage reactive system; distillation, correlation.

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1. Introduction

Distillation has been studied as a mass transfer phenomena where diffusion occurs through the liquid- vapor interface. A different approach to the modeling of packed columns, particularly applicable to multicomponent distillation, was developed and applied in full-scale tests in papers [1-6]. They put forward the concept of mass transfer section and defined vaporization efficiencies to compensate for the deviation of each section from an ideal stage.

Ruckenstein [7] solved the transport equations in the liquid phase without using the two-film model. This was a simultaneous treatment of heat and mass transfer, but confined to the liquid phase. Dutkai-Rukenstein [8] abandoned the idea of thermal distillation and modeled the packed column using only overall mass transfer coefficients. The overall mass transfer efficiency was investigated by Savkovic-Stevanovic et.al.[9].

Industrial separation processes involving acetic acid continue to be of considerable interest. Mass transfer between the liquid and vapor phase of the systems with association in a distillation column was studied [10]. The effects of association on the HTU in laboratory and pilot-plant packed distillation columns are investigated in the paper Savkovic-Stevanovic [11].

In this paper the substance transfer coefficients and height of transfer units are determined, using effective diffusion coefficients and chemical reaction rate. Method for substance transfer coefficients determination was derived by fitting working curve and vapor-liquid equilibrium curve to the experimental data.

2. Mass transfer phenomena in a distillation column with reaction esterification

Let assume, in a reactive distillation packed column concentration gradient is changed only in z direction elements Δz_1, Δz_2, Δz_3, …., Δz_n counting from the top to the bottom. Phase equilibrium between vapour and liquid phases for component i, at the same point is,

$$f_i^V = E_i\ f_i^L \tag{1}$$

where E$_i$ vaporization efficiency at the point. Analogously, for any section Δz$_j$ will be:

$$f_{ji}^V = E_{ji}\, f_{ji}^L \tag{2}$$

where E_{ji} so called vaporization efficiency for any element Δz$_{ji}$. For equilibrium conditions when vapor and liquid phases pressure and temperatures are equal then,

$$y_{ji} = E_{ji} x_{ji} \gamma_{ji} (f_{ji}^V / f_{ji}^L) \tag{3}$$

If the both vapor and liquid phases can be considered as ideal solution, then can be denoted with $K_{ji} = f_{ji}^V / f_{ji}^L$.

Material balance for steady state conditions:
Material balance for the vapor phase of the element Δz$_{ji}$ is,

$$G_{j+1} - G_j + \int_{z_j}^{z_{j=1}} \sum_{i-1}^{M} N_i dz + r_j = 0 \tag{4}$$

and for the liquid phase,

$$L_{j-1} - L_j - \int_{z_j}^{z_{j=1}} \sum_{i-1}^{M} N_i dz + r_j = 0 \tag{5}$$

Energy balance for steady state conditions:
Energy balance for the vapor phase of the element Δz$_{ji}$ is,

$$G_{j+1} H_{j+1} - G_j H_j + \int_{z_j}^{z_{j=1}} \sum_{i-1}^{M} N_i dz + (\Delta H)_r r_j - \int_{z_j}^{z_{j=1}} Q_G dz = 0 \tag{6}$$

Energy balance for the liquid phase which including liquid phase, liquid film, interphase and vapour film and reaction heat of the element Δz$_{ji}$ is,

$$L_{j-1} h_{j-1} - L_j h_j - \int_{z_j}^{z_{j=1}} \sum_{i-1}^{M} N_i dz + (\Delta H)_r r_j + \int_{z_j}^{z_{j+1}} Q_G dz = 0 \tag{7}$$

3. Chemical reaction rate

For esterification reaction general kinetic model [12-13] is:

$$CH_3COOH + C_2H_5OH \underset{k'}{\overset{k}{\Leftrightarrow}} CH_3COOC_2H_5 + H_2O \tag{8}$$

(A) (B) (C) (D)

The reaction can be resulted in the following equivalent form:
$v_A(A) + v_B(B) + v_C(C) + v_D(D) = 0$, where $v_A = -1, v_B = -1, v_C = +1, v_D = +1$.

$$\frac{dc_A}{dt} = \frac{dc_B}{dt} = (-k_e c_A c_B + k_{re}^{'} c_C c_D) \tag{9}$$

$$\frac{dc_C}{dt} = \frac{dc_D}{dt} = (k_e c_A c_B - k_{re}^{'} c_C c_D) \tag{10}$$

Then, the reaction rate is given by eq.(11)

$$r = k_e c_A c_B - k_{re}^{'} c_C c_D \tag{11}$$

where $k_e = 58.7E - 03\exp(-17.46/T)$; $k'_{re} = 22.1E - 03\exp(-16.53/T)$; $k_r = k_e - k'_{re}$

Specific reaction constants for esterification and reesterification, vapor –liquid equilibrium data and activity coefficients have taken from paper [13-15]. In this paper method for substance transfer coefficients in a reactive distillation column was developed. In previously papers effects of reaction yields and kinetics ethyl-acetate formation were investigated [13].

4. Mass transfer rate

Mass transfer rate between vapor and liquid phase can be defined as follow:

$$dN_i = G dy_i = L dx_i \tag{12}$$

$$dN_i = k_G a(y_i - y_{ib})Sdz = k_L a(x_{ib} - x_i)Sdz \tag{13}$$

Since, inter phase y_b and x_b uncertain for given location it is more convention to use over all component transfer coefficient as following:

$$dN = k_{OG} a(y - y^*)Sdz = k_L a(x^* - x)Sdz \tag{14}$$

and combining eqs.(13)-(14) is obtained:

$$\int_0^z dz = G\int_{y1}^{y2} \frac{dy}{k_{OG} aS(y_i - y_i^*)} = L\int_{x1}^{x2} \frac{dx}{k_{OL} aS(x_i^* - x_i)} \tag{15}$$

By integration between top and bottom of the column can determine total column height Z.

$$Z = \frac{G}{k_{OG} aS}\int_{y_B}^{y_D} \frac{dy}{y_i - y_i^*} = \frac{L}{k_{OL} aS}\int_{x_B}^{x_D} \frac{dx}{x_i^* - x_i} \tag{16}$$

Integral in eq.(16) defines NTU –Number of Transfer Unit and Z/NTU is equal HTU-Height of Transfer Unit.

Relationships between overall and individual height of transfer unit are given by eqs.(17)-(18),

$$(HTU)_{OG} = (HTU)_G + \frac{mG}{L}(HTU)_L \tag{17}$$

$$(HTU)_{OL} = (HTU)_L + \frac{L}{mG}(HTU)_G \tag{18}$$

where mG/L and L/mG $(m=K)$ are absorption and desorbtion factors.

Relationship between overall and individual substance transfer coefficients are given by eqs.(19)- (20).

$$\frac{1}{k_{OG}} = \frac{1}{k_G} + \frac{m}{k_L} \tag{19}$$

$$\frac{1}{k_{OL}} = \frac{1}{k_L} + \frac{1}{mk_G} \tag{20}$$

5. Experimental

The experimental setup has shown in Fig.1. The experimental data were obtained in a ordinary glass "Normag" distillation column with a packing height of 1000 mm and a diameter of 33 mm. The average diameter of packing particle Amberlite-120 was 0.81 mm. The bed void fraction was 0.6, and the specific surface of packing 7.056 mm^2/ mm^3.

The batch distillation unit is controlled by the acquisition block. "Normatron" was connected for reflux flow rate control over microprocessor. Sensor for pressure drop and temperature sensors Pt-100 were used.

The experiments were carried out by batchwise distillation operation and were semi-continuous in adiabatic conditions. The compositions of the distillate and the bottom product were determined by Gas Chromatograph.

The esterification reaction was carried out at the atmospheric pressure. Holdup on each stage was 1 mole, for total condenser and reboiler 2 moles. The distillation was performed at different flow rates through the column. The hydrodynamic characteristics with a cationic ion exchanger were determined as shown in Fig.2 . The optimal flow rate through the column was examined.

6. Correlation models

Height of transfer units were correlated by Sherwood-Holloway and Zuiderweg correlation models eqs.(21)-(24)[16-18],[22]. Substance transfer coefficients were modelled by Sherwood-Holloway and Onda-Takeuchi-Okumoto correlation models [19-21],[22].

The original correlation models was modified for chemical reaction rate by Savkovic-Stevanovic-Mosorinac eqs.(21)-(27).

Height of transfer unit:

Sherwood-Holloway:

$$(HTU)_L = B_1(1/k_r)(L/\mu_L)^{0.25} Sc_L^{0.5} \qquad (21)$$

$$(HTU)_G = B_2(1/k_r)(G^{0.31}/L^{0.33}) \qquad (22)$$

Zuiderweg:

$$(HTU)_L = C_1(1/k_r)W^{0.27} d_p^{\;0.33} D_L^{-0.5} g^{-0.17} \qquad (23)$$

$$(HTU)_G = C_2(1/k_r)\mathrm{Re}_G^{\;0.4} Sc_G^{0.67} W_L^{-0.56} \qquad (24)$$

For substance transfer coefficient:

Sherwood-Holloway:

$$(k_L a)k_r / D_L = \frac{1}{B}\left(\frac{L}{\mu_L}\right)^{1-n} Sc^{).5} \qquad (25)$$

where $a = S_p / V_p(1-\varepsilon)$.

Onda-Takeuchi and Okumoto:

$$(k_L k_r / c_T)(\rho_L/\mu_L\ g)^{1/3} = C_3(L/a_w\mu_L)^{2/3}(\mu_L/\rho_L D_L)^{-0.5}(a_t D_p)^{0.4} \qquad (26)$$

$$(k_G k_r a_t D_G R_G T / p) = C_4(G/a_t\mu_G)^{0.7}(\mu_G/\rho_G D_G)^{1/3}(a_t D_p)^{-2.0} \qquad (28)$$

Where: $We = L^2/\rho_L \sigma a_t$, $Fr = L^2 a_t/\rho_L^{\;2} g$, $\mathrm{Re} = L/a_t\mu_{L.}$

Diffusion coefficients were calculated according to equations Fuller et al.[23], Lusis Ratsliff [24], Leffer-Cullinan [25-26], Kooijman H.A, R.Taylor [27] and Savkovic-Stevanovic [28].

An algorithm was derived according to Eqs.(13)- (20). Program module was developed in Fortran programming language using numerical integration method [14]. For parameters determination in correlation models based on least squares method an algorithm was derived and corresponding program modules [15].

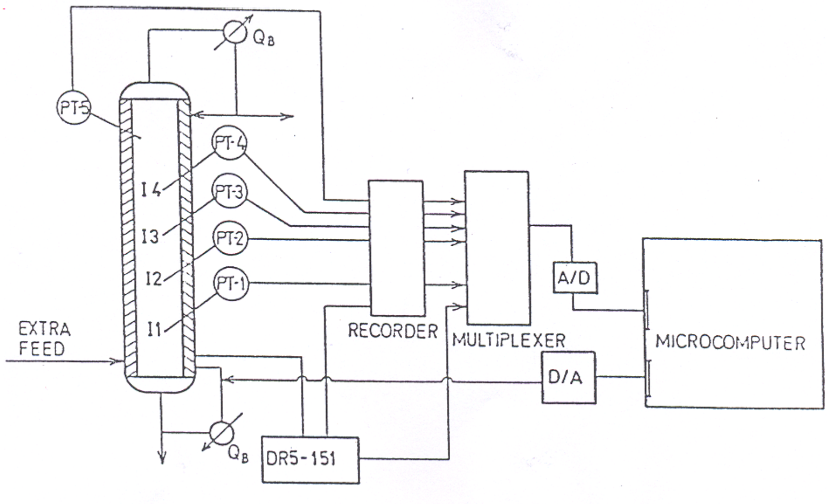

Fig.1 Experimental set-up

The parameters values in correlation models for HTU are given in Table 1. The parameters for substance transfer coefficient correlations are given in Table 2.

Table 1. The parameters values for the examined correlations for HTU

Correlation	Gas phase	Liquid phase
Sherwood -Holloway	B1=9.906E01	B2=2.297
Zuiderweg	C1=2.297	C2=2.721E03

Table 2. Parameters values for substance transfer coefficients for the examined correlations

Correlation	Gas phase	Liquid phase
Sherwood -Holloway	-	B=2.0548E-10
Onda-Takeuchi-Okumoto	C_3=5.742E03	C_4=1.464E013

7. Results and discussion

The obtained results are presented in Figs.2-10. The pressure drop vs. vapor velocity has shown in Fig.2. The optimal flow rate for the examined column was w=1.8m/s. The experimental data were given under total reflux ($R = \infty$).

The obtained results for HTU and mass transfer coefficients for variety flow rate through the column are given in Fig.3- Fig.10. Fig.3 shows the experimental values for overall HTU for ethyl- acetate in the both liquid and gas phases vs. liquid flow rate.

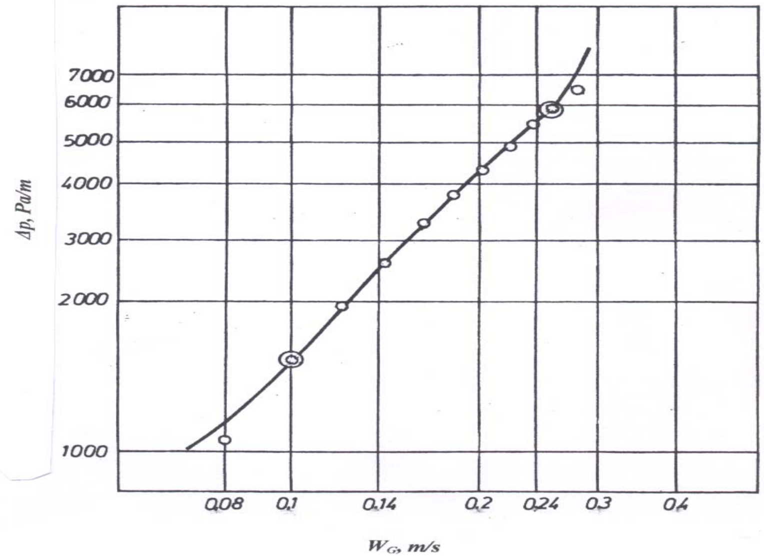

Fig.2 Pressure drop vs. vapor velocity ($R = \infty$)

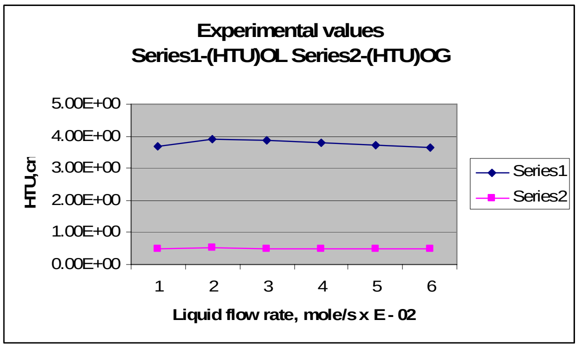

Fig.3 Overall HTU for ethyl acetate in the liquid and the gas phase vs. liquid flow rate

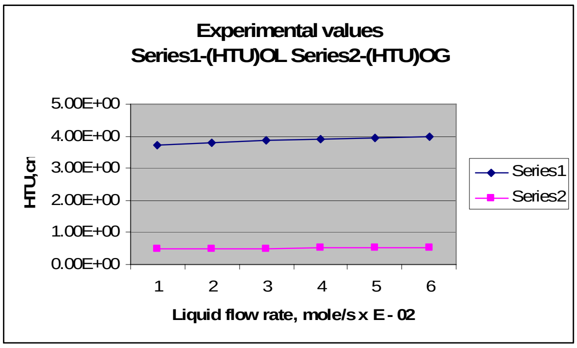

Fig.4 Overall HTU for ethyl alcohol in the liquid phase and the gas phase vs. liquid flow rate

Fig.4 shows the experimental values HTU for ethanol in the both liquid and gas phase as a function of liquid flow rate.

In Fig.5 has shown ethyl-acetate transfer coefficients for the both liquid and gas phase in a function of liquid flow rate. Fig.6 shows overall values for ethanol transfer coefficients from experiments.

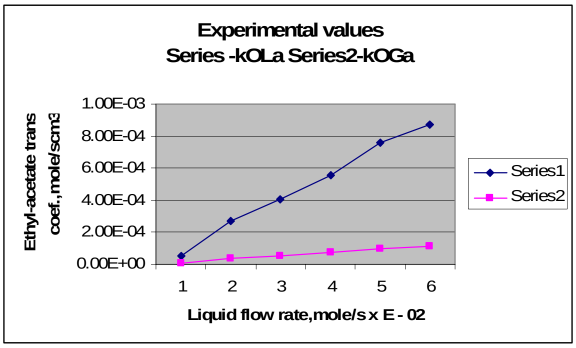

Fig. 5 Overall ethyl-acetate transfer coefficients vs. liquid flow rate

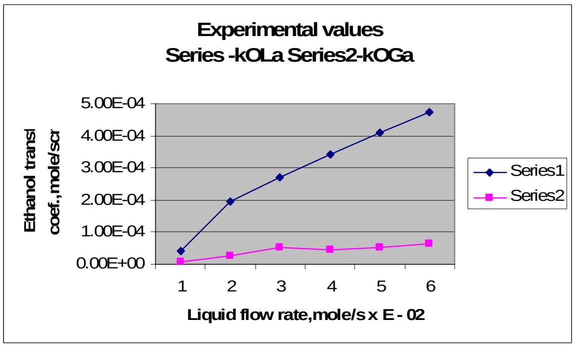

Fig.6 Overall ethyl alcohol transfer coefficients vs. liquid flow rate

In Fig.7 has shown calculated values for individual $(HTU)_L$ and $(HTU)_G$ according to Sherwood-Holloway correlation. Fig.8 shows the comparative values for ethyl-acetate transfer coefficients k_L according to Sherwood-Holloway and Onda,Takeuchi and Okumoto correlations.

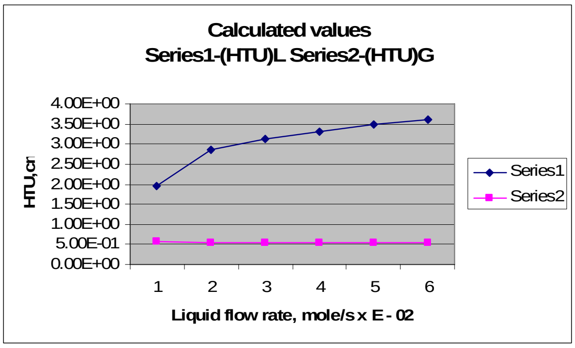

Fig.7 $(HTU)_L$ and $(HTU)_G$ for ethyl-acetate by Sherwood-Holloway correlation

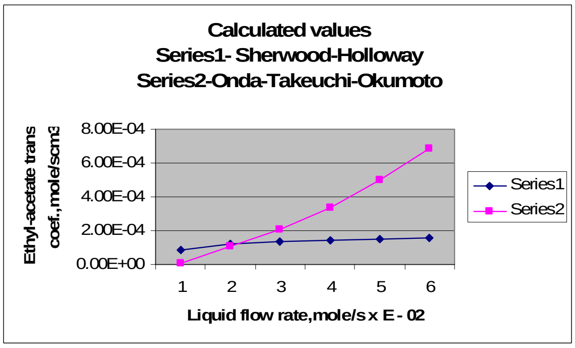

Fig.8 Ethyl-acetate liquid phase transfer coefficient k_L vs. liquid flow rate calculated by Onda-Takeuchi-Okumoto and Sherwood-Holloway correlations

Fig.8 shows better sensitivity Onda-Takeuchi and Okumoto correlation than Sherwood-Holloway for varies liquid flow rate through the column. Fig.9 has shown HTU values for ethyl-acetate calculated according to Zuiderweg correlation.

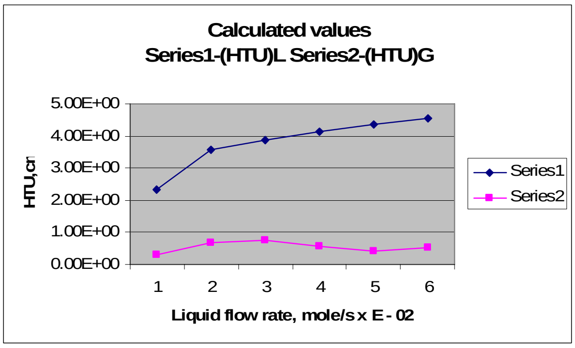

Fig.9 $(HTU)_L$ and $(HTU)_G$ for ethyl-acetate calculated according to Zuiderweg correlation vs. liquid flow rate

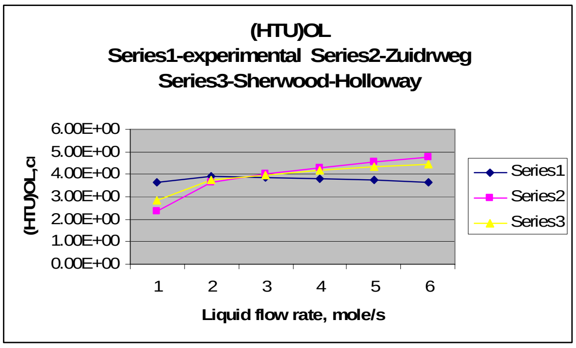

Fig.10 The experimental and calculated values for (HTU)OL for ethyl-acetate

Comparison these values with those from Fig.7 obtained by Sherwood-Holloway correlation shows similarity. Zuiderweg correlation model gives better sensitivity with flow rate chaining.

Comparison calculated values for (HTU)OL with those experimental has shown in Fig.10. Fig.10 shows better fitting Sherwood Holloway correlation than Zuiderweg correlation to the experimental data.

8. Conclusion

The substance transfer coefficients and height of transfer units are examined, using effective diffusion coefficients and specific chemical constant. The substance transfer coefficients determination method was derived by fitting working curve and vapor-liquid equilibrium curve to the experimental data.

Efficiency of the substance transfer by HTU/NTU methods for quaternary systems were investigated. The overall, individual and component transfer coefficients were determined.

Scherwood-Holloway and Zuiderweg correlation models for HTU/NTU and Scherwood-Holloway and Onda-Takeuchi-Okumoto models for substance transfer coefficients were studied.

The obtained results show good agreement between simulated and experimental data. The obtained results in this paper can be applied in others multistage, multiphase and multi-component separation domain.

Notation

A	interfacial surface per unit volume, cm^2/cm^3
a_t	total surface area of packing per unit volume, cm^2/cm^3
B_1,B_2	constants
$C_T,C_1,C_2,$ C_3,C_4	constants
D	fluid diffusivity, cm^2/s
d_c	column diameter, cm
D_L, D_G	diffusivity of the liquid and gas phase, respectively, cm^2/s
D_p	diameter of packing, cm
E	vaporization efficiency
F	fugacity
G	gas flow rate, mole/s
g	gravitational acceleration, cm/s^2
H	enthalpy of the liquid phase, J/mole
H	enthalpy of the vapour phase, J/mole
HTU	Height of transfer unit, cm
$(HTU)_L$, $(HTU)_G$	height of transfer unit over the liquid and gas phase, respectively, cm
K	equilibrium constant
k_r	specific chemical reaction constant, $l\ mol^{-1}\ s^{-1}$ ($=k_e-k'_{re}$)
k_e	esterification constant, $l\ mol^{-1}\ s^{-1}$
k'_{re}	reesterification constant, $l\ mol^{-1}\ s^{-1}$
k_L k_G,	individual transfer coefficient for the liquid and the gas phase, respectively, mol/cm^3 s
k_{OG}, k_{OL},	overall substance transfer coefficient, mol/cm^3 s
L	liquid flow rate, mol/s
M	total number of component
N	total number of molecules
N	constant
NTU	Number of transfer unit
Q	heat
R	reflux ratio
R_G	gas constant
Re	Reynolds number ($=\rho d_c w/\mu$)

Sc	Schmidt number ($=\mu/rD$)
Sh	Sherwood number ($=kd_c$/D)
r_j	reaction rate, mol/s
S	radial column surface, cm^2
S_p	packing surface, cm^2
T	temperature, K
y	vapor composition
y^*	equilibrium composition
x	liquid phase composition
V	volume,cm^3
W	gas phase velocity, cm/s
Z	column height, cm

Greek symbols

$\mu -$ fluid viscosity, Pas

ρ -density, g/cm^3

$\sigma - surface tension, N/m$

$\varepsilon - bedvoid \quad fraction$

Subscript

A	acetic acid	G	gel
C	ethanol	L	liquid
B	ethyl-acetate	OG	overall liquid phase
D	water	OL	overall gas phase
G	gas	P	packing

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