

Substance transfer modelling in multistage, multicomponent, reactive distillation

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Abstract

In this paper substance transfer coefficients modelling method for multistage, multiphase and multicomponent system was presented. The determination of the substance transfer coefficients were performed by experiments and computer simulation. The overall, individual and component substance transfer coefficients were determined. Efficiency of the mass transfer by HTU/NTU methods for quaternary systems were investigated. Component transfer coefficients in distillation column with reaction esterification of the ethanol and acetic acid were studied. The ethyl-acetate, the ethanol and the acetic acid transfer coefficients were determined.

Keywords: Component mass transfer coefficients, HTU/NTU efficiency, modeling of chemical rate and mass transfer rate, reactive distillation.

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 by Holland et.al.,1970;Bassiyoni,1970;Holland et.al.,1971;McDaniel et.al.,1970;McDaniel and Holland,1970;Rubac et.al,1970). 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

,1970) 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,1971 abandoned the idea of thermal distillation and modelled the packed column using only overall mass transfer coefficients. The overall mass transfer efficiency was investigated by Savkovic-Stevanovic et.al.,1977;Savković-Stevanović,1980.

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 reaction in a distillation column was studied by Savkovic-Stevanovic,1985;1992. The effects of association on the HTU (Height of Transfer Unit) in laboratory and pilot-plant packed distillation columns are investigated in paper Savkovic-Stevanovic,1992.

In this paper the mass transfer coefficients are modelled, using effective diffusion coefficients and specific chemical reaction constant. Method for mass transfer coefficients determination was derived by fitting working curve and vapor-liquid equilibrium curve to the experimental data (Ivanović-Knežević,2007).

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

Let assume, in a distillation packed column concentration gradient is changed only in z direction elements $\Delta z_1, \Delta z_2, \Delta z_3, \dots, \Delta z_n$ counting from the top to the bottom.

Phase equilibrium between vapour and liquid phases for component i, at the same point is,

$$f_i^V = E_i f_i^L \quad (1)$$

where E_i vaporization efficiency at the point. Analogously, for any section Δz_j will be:

$$f_{ji}^V = E_{ji} f_{ji}^L \quad (2)$$

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

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

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

For steady state conditions:

Material balance for the vapor phase of the element Δz_{ji} is,

$$V_{j+1} - V_j + \int_{z_j}^{z_{j+1}} \sum_{i=1}^M N_i dz + v_j = 0 \quad (4)$$

and for the liquid phase,

$$L_{j-1} - L_j - \int_{z_j}^{z_{j+1}} \sum_{i=1}^M N_i dz + v_j = 0 \quad (5)$$

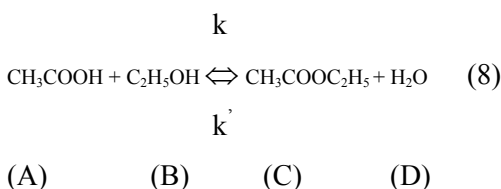
Energy balance for the vapor phase of the element Δz_{ji} is,

$$V_{j+1} H_{j+1} - V_j H_j + \int_{z_j}^{z_{j+1}} \sum_{i=1}^M N_i dz + (\Delta H)_r v_j - \int_{z_j}^{z_{j+1}} Q_G dz = 0 \quad (6)$$

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 analogical eq.(6).

3. Chemical reaction rate

For esterification reaction general kinetic model Savkovic-Stevanovic et.al.,1986;1992 is:



$$\frac{dc_A}{dt} = \frac{dc_B}{dt} = (-k_j c_A c_B + k'_j c_C c_D) \quad (9)$$

$$\frac{dc_C}{dt} = \frac{dc_D}{dt} = (k_j c_A c_B - k'_j c_C c_D) \quad (10)$$

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

$$v_j = k_j c_A c_B - k'_j c_C c_D \quad (11)$$

Specific reaction constants for esterification and reesterification are given in the Appendix (Table A.1).

Vapor –liquid equilibrium constants are given in the Appendix Table A.2. Coefficients activity have taken from paper Savkovic-Stevanovic et.al.,1986;1992.

4. Mass transfer rate

Mass transfer rate between vapor and liquid phase according two film theory can be defined as follow:

$$dN_i = V dy_i = L dx_i \quad (12)$$

$$dN_i = k_G a(y_i - y_{ib}) S dz = k_L a(x_{ib} - x_i) S dz \quad (13)$$

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

$$dN = k_{OG} a(y - y^*) S dz = k_L a(x^* - x) S dz \quad (14)$$

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

$$\int_0^Z dz = V \int_{y_1}^{y_2} \frac{dy}{k_{OG} a(y - y_i^*)} = L \int_{x_1}^{x_2} \frac{dx}{k_{OL} a(x_i^* - x)} \quad (15)$$

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

Integral 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,

$$(HTU)_{OG} = (HTU)_G + \frac{mV}{L} (HTU)_L \quad (16)$$

$$(HTU)_{OL} = (HTU)_L + \frac{L}{mV} (HTU)_G \quad (17)$$

where mV/L and L/mV ($m=K$) are absorption and desorbition factors.

5. Experimental setup

The experimental data were obtained in a distillation column (Figure 1) with the 33

mm diameter, the height of packing 1000 mm and the specific surface of packing $7.056 \text{ mm}^2/\text{mm}^3$. The average diameter of packing particle Amberlite-120 was 0.8 mm. 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 products composition were determined by Gas Chromatograph.

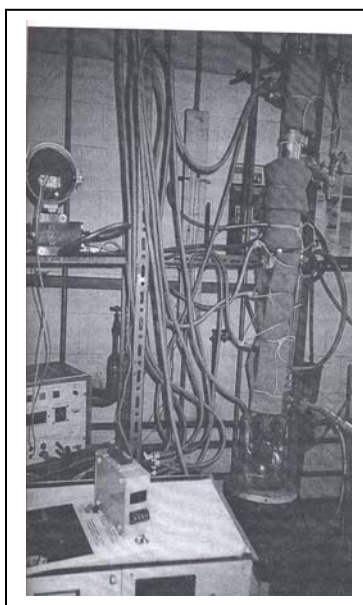


Figure 1. Distillation column with data acquisition system

6. Computational methods

In this paper method for component transfer coefficients in a laboratory reactive distillation column. An algorithm was derived according to Savkovic-Stevanovic et.al.,1986;1992;Ivanović-Knežević,2007. Program's module was developed in Fortran programming language using numerical integration method.

In previously papers Savkovic-Stevanovic et.al.,1986; 1992 effects of reaction yields and kinetics ethyl-acetate formation were investigated.

7. Results and discussion

The obtained results for substance transfer coefficients and NTU/ HTU for variety flow rate through the column are given in Figure 2-Figure 6. Experimental data were given under total reflux.

Figure 2 shows HTU for ethyl acetate vs. liquid flow rate L.

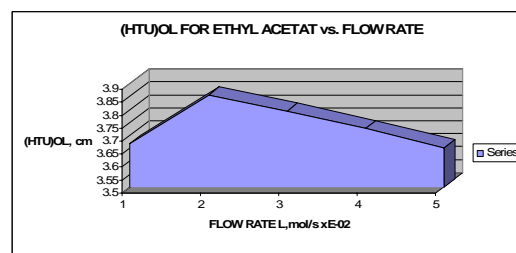


Figure 2. Height of transfer units vs. liquid flow rate through the column

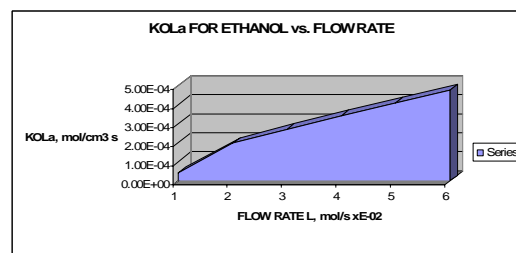


Figure 3. Ethanol transfer coefficients in dependence of the liquid flow rate through the column

Figure 4 shows ethyl-acetate transfer coefficients as a function liquid flow rate. In

Figure 5 acetic acid transfer coefficients have shown.

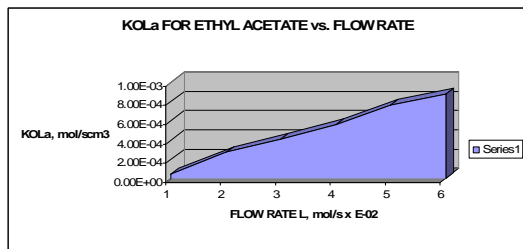


Figure 4. Ethyl-acetate transfer coefficients as function of the liquid flow rate through the column

Water transfer coefficients as function of the liquid flow rate has shown in Figure 6.

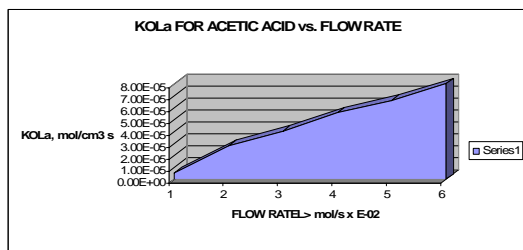


Figure 5. Acetic acid transfer coefficients vs. liquid flow rate through the column

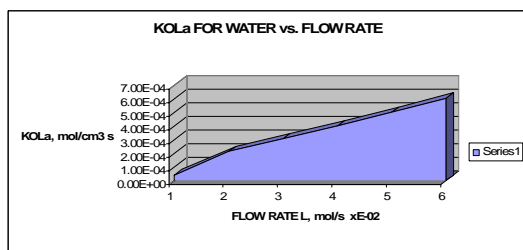


Figure 6. Water transfer coefficients vs. liquid flow rate through the column

8.Conclusion

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

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

The obtained results can be applied in others multistage, multiphase and multicomponent separation domain.

Appendix

Specific reaction rate constants for esterification and reesterification reaction second order are:

$$k_j = k_0 \exp(-E/RT) \text{ Lmol}^{-1} \text{ min}^{-1} \quad (\text{A1.1})$$

Kinetic parameters for uncatalysed and catalysed reaction are given in Table A.1.

Table A1. Kinetic parameters

Reaction	Parameter $k_0, \text{Lmol}^{-1}\text{s}^{-1}$ $E, \text{J/mol}$
Catalysed esterification	$k_0=29.000 \times 10^{-3}$ $E=7150$
Catalysed reesterification	$k_0=7.380 \times 10^{-3}$ $E=7150$
Uncatalysed esterification	$k_0=58.700 \times 10^{-3}$ $E=17.460$
Uncatalysed reesterification	$k_0=22.100 \times 10^{-3}$ $E=16.530$

Vapor liquid equilibrium constants are given in Table A.2

Table A.2 Vapor –Liquid Equilibrium Data

Component	VLE ratio
A-Acetic acid	$K=2.25 \times 10^{-2} \quad t > 74.45$ $1.666 \quad t < 74.45$
	$K=0.001$ $t < 74.45$
B-Ethanol	$\log K = -2.3 \times 10^3/T + 6.58825$
C-Ethyl acetate	$\log K = -2.3 \times 10^3/T + 6.48351$
D-Water	$\log K = -2.3 \times 10^3/T + 6.74151$

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Notation

A-acetic acid

a- packing specific surfaces, cm^2/cm^3

C-ethyl-acetat

D-water

E-vaporization efficiency

f-fugacity

H-enthalpy of the liquid phase. J/mole

h- enthalpy of the vapor phase. J/mole

HTU- Height of transfer unit

K- equilibrium constant

k-specific chemical reaction constant, $\text{L mol}^{-1} \text{min}^{-1}$

k_{OG} , k_{OL} , mass transfer coefficient, $\text{mol}/\text{cm}^2 \text{s}$

L-distillate flow rate, mole/s

M-total number of component

N- total number of molecules

NTU-Number of transfer unit

Q-heat

S-radial column surface, cm^2

T-temperature, K

t-temperature, °C

y- vapor composition

y^* - equilibrium composition

x-liquid phase composition

V-bottoms flow rate, mole/s

z- column height, cm

Superscript

V-vapor

L-liquid

Subscript

A-acetic acid

B-ethanol

b-bounded film

C-ethyl-acetat

D-water

V-vapor

L-liquid

i- any component

j-any section

r-reaction

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IZVOD

MODELOVANJE PRENOSA SUPSTANCE U VIŠEFAZNOJ, VIŠEKOMPONENTNOJ REAKTIVNOJ DESTILACIJI

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U ovom radu data je metoda modelovanja koeficijenata prenosa materije za višestupnjevite, višefazne i višekomponentne sisteme. Koeficijenti prenosa materije određivani su pomoću eksperimenta i računarskim simulacijama. Određivani su ukupni, individualni i komponentni koeficijenti prenosa materije. Ispitivana je efikasnost prenosa materije kvaternernog sistema pomoću HTU/NTU metoda. Proučavani su komponentni koeficijenti prenosa u destilacionoj koloni sa reakcijom esterifikacije etanola i sirćetne kiseline. Određivani su koeficijenti prenosa etanola, etil-acetata, sirćetne kiseline i vode.

Ključne reči: transfer coefficients, distillation, esterification, HTU/NTU.

