MASS TRANSFER IN BINARY DISTILLATION OF NITROGEN-OXYGEN AND ARGON-OXYGEN SYSTEMS IN A WETTED-WALL COLUMN

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The measurements of mass fluxes in binary distillation of the nitrogen-oxygen and argon-oxygen systems in a wetted-wall column were made under total reflux conditions for a wide range of turbulent flows.

The observed diffusion fluxes of each components in binary distillation were found to be proportional to their concentration driving forces, whereas the observed mass fluxes were not. A new correlation for vapor phase diffusion fluxes in the nitrogen-oxygen and argon-oxygen systems was proposed.

Introduction

Cryogenic air distillation has been widely applied to industrial production of nitrogen, oxygen and argon. Although some studies have been made on mass transfer in air separation processes by staged contactors, relatively few study on mass transfer by continuous contact equipment is known. And there is no literature which deals with air distillation as a simultaneous heat and mass transfer process.

Recently Agrawal *et al.* (1993) made an experimental approach to mass transfer in a packed distillation column with structured packing for nitrogen-oxygen and argon-oxygen systems and proposed a correlation for overall gas phase mass transfer coefficient for a nitrogen-oxygen system. Furthermore they reported that their correlation is not applicable for prediction of separation performance of argon-oxygen systems.

Kosuge *et al.* (1990, 1991) made an experimental approach to heat and mass transfer in binary distillation of the acetone-ethanol, acetone-methanol and methanol-ethanol systems and ternary distillation of the acetone-methanol-ethanol system by a packed column with random packing and proposed a correlation for vapor phase diffusion fluxes. Olaño *et al.* (1995) also developed a mass transfer correlation for distillation using the structured packing in terms of dimensionless diffusion flux and showed that a theoretical analytical approach for mass and heat transfer in distillation for a wetted-wall column was applicable for the structured packing. However, these studies have been limited to the vapor phase Reynolds number range which is lower than that

needed in industrial air separation processes.

The contacting apparatus chosen in this study was a wetted-wall column. The purpose of this work is to make an experimental approach to heat and mass transfer in binary cryogenic distillation of nitrogen-oxygen and argon-oxygen systems in a wetted-wall column under total reflux conditions for a wide range of turbulent flows, and to develop a new correlation for prediction of separation performance of air distillation.

1. Experimental Apparatus and Procedures

1.1 Experimental apparatus

Figure 1 shows a schematic diagram of the experimental apparatus. The test column was a 304 stainless steel wetted-wall column, 25.1 mm in inner diameter, and 550 mm long. The two pressure taps were equipped at 108.0 mm from the top and at 25.0 mm from the bottom, respectively, for measurements of operating pressures of the column. A horizontal vapor inlet tube, 9.0 mm in outer diameter, with a 6.0 mm diameter hole was equipped at the bottom of the column. Reflux liquid was uniformly supplied around the wall of the column through a specially designed liquid distributor*. Details of the test column were shown in Fig. 2. The reboiler was a nitrogen-gas heated U-tube heat exchanger with a heat transfer surface of 0.19 m², of which the maximum capacity was 2.2×10⁻³ m³. Heat supply to the reboiler was adjusted by controlling flow rates of nitrogen-gas to the reboiler. The condenser was a vertical tube total condenser with condensing surface area of 0.19 m², of which a maximum oxygen throughput was 2.5×10⁻³ kg/s. The test column, reboiler, total condenser and major measuring devices

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* A preliminary visual observation with R-11 showed good wetting of the wetted-wall in wide range of liquid flow rates.

Fig. 1 Schematic diagram of experimental apparatus

Fig. 2 Schematic diagram of wetted-wall column

Table 1 Ranges of variables for binary distillation using a wetted-wall column

System	y_{Ob} [—]	Re_G [—]	Sc_{Gs} [—]	P_b [kPa]
Nitrogen-Oxygen	0.10 – 0.72	2960 – 10790	0.69 – 0.70	110 – 182
Argon-Oxygen	0.56 – 0.92	3950 – 9600	0.70 – 0.73	107 – 125

were kept in a vacuum 558.8 mm in outer diameter, in a 3365 mm-long cold box with a liquid nitrogen-insulated wall, which is shown in Number 4 of Fig. 1.

Distillation runs were made under total reflux conditions and at nearly atmospheric pressures. The measurements were carried out after the liquid level of the reboiler and condenser were at their steady state.

1.2 Measurements

1.2.1 Vapor flow rates, concentrations, temperature and pressure

The top and bottom vapor flow rates, V_t , V_b , were measured by two turbine flow-meters (Japan Flow Controls, Model FMC-8CM1.2-G437) with an accuracy better than 1%. The top and bottom vapor oxygen concentrations, ω_{GOB} , ω_{GOt} were measured by the zirconia oxygen analyzers (Toray Engineering, Model LC-700 H) with an accuracy better than 2 mole%. Vapor and liquid temperatures at the top and bottom were monitored with the 1.6 mm-outer diameter sheathed Pt-resistance thermometers (JIS Class A). Pressures were mea-

sured by the absolute pressure transducers (Setora Systems, Model 204), which had an accuracy of 0.11%.

1.2.2 Mass fluxes

The average vapor phase mass fluxes of each component, N_i , were calculated from the top- and bottom-vapor flow rates and concentrations as:

$$N_i = \frac{V_b \omega_{Gib} - V_t \omega_{Git}}{\pi DL} \quad (i = 1, 2) \quad (1)$$

where the interfacial area was taken equal to the internal surface area of the wetted-wall column*.

1.3 Vapor-liquid equilibria and physical properties

Vapor-liquid equilibria of the nitrogen-oxygen and argon-oxygen systems were estimated from the

* The effect of the liquid film thickness on the interfacial area was negligible because the liquid film thickness estimated from Nusselt's equation was less than 0.4% of a wetted-wall column inner diameter.

Fig. 3 Vapor phase mass fluxes for nitrogen-oxygen and argon-oxygen systems

vapor pressures of pure components by Riedel's equation, from the liquid phase activity coefficients by Two-suffix Margules equation and from the vapor phase fugacity coefficients by the virial equation of state with the second and third virial coefficients, where Riedel and Margules constants by Wilson *et al.* (1965) were used. The binary diffusion coefficients were estimated by Hirschfelder's equation (Reid *et al.*, 1987). The viscosities of pure vapors were estimated by NBS's correlation (1980) and viscosities of vapor mixture were estimated by Wilke's method (Reid *et al.*, 1987).

1.4 Ranges of variables

Binary distillation measurements were carried out for the nitrogen-oxygen and argon-oxygen systems under total reflux conditions over wide ranges of vapor flow rates and concentrations. The ranges of variables for measurements are shown in Table 1.

2. Results and Discussion

2.1 Dimensionless mass fluxes

It is assumed that the simultaneous heat and mass transfer processes of distillation are vapor phase controlled in this study (Kayihan *et al.*, 1977, Ito and Asano, 1982, Kosuge *et al.*, 1985).

The mass transfer rates have been generally described in terms of Sherwood number defined by the following equation as a dimensionless mass flux.

$$Sh_{Gi} = \frac{N_i D}{\rho_G D_{G12} \Delta \omega_{Gi}} \quad (i = 1, 2) \quad (2)$$

where $\Delta \omega_{Gi}$ is the average concentration driving force defined as:

Fig. 4 Effect of concentration driving force on mass flux

$$\Delta \omega_{Gi} = \frac{1}{\omega_{Git} - \omega_{Gib}} \int_{\omega_{Gib}}^{\omega_{Git}} (\omega_{Gi} - \omega_{Gsi}) d\omega_{Gi} \quad (i = 1, 2) \quad (3)$$

In this study the $\Delta \omega_{Gi}$ is calculated from the logarithmic mean approximation of top and bottom concentration driving forces. Figure 3 shows the average vapor-phase Sherwood number of oxygen observed in the nitrogen-oxygen and argon-oxygen systems, where a solid line shows the correlation of Agrawal *et al.* (1993). The ordinate is the dimensionless mass flux of oxygen, $Sh_{GO}/Sc_{GO}^{1/3}$. The abscissa is the vapor phase Reynolds number. The figure shows an irregular scattering of the data. Negative values of the Sherwood number were observed in the case of bottom oxygen concentration of 92%. This may be due to mass transfer in an opposite direction which is expected from the driving force. The dimensionless mass fluxes are different for each systems. This is due to the effect of the normal component of the surface velocity caused by simultaneous heat and mass transfer. Heat transfer through the vapor-liquid interface is due to the latent heat exchange, convective heat transfer and heat input through the wall. The figure indicates that Agrawal's correlation can not be applied to the present data of the argon-oxygen system. This trend agrees with their report in which the correlation developed from a nitrogen-oxygen system is not applicable for prediction of the separation performance of argon-oxygen system. The reason may be due to the fact that the interaction between heat and mass transfer is neglected in their correlation. These results may indicate that the dimensionless mass fluxes are not

Fig. 5 Effect of concentration driving force on diffusion flux

suitable for correlating binary distillation data in the wetted-wall column. To investigate this in more detail, the mass and diffusion fluxes will be discussed in the following section.

2.2 Mass and diffusion fluxes

Figure 4 shows the effects of concentration driving forces on the observed average vapor phase mass fluxes for each components at nearly constant vapor phase Reynolds number. The abscissa is the average concentration driving forces. The observed mass fluxes for each component were not zero at zero-driving force, although the observed mass fluxes were almost linear to their concentration driving forces. This indicates that mass transfer occurs at zero-driving force. Some observed mass fluxes show negative values even though the driving forces were positive. This causes the negative values of the Shewood number. This may be due to the effect of convective mass fluxes caused by the mass transfer of each component.

By considering the following well-known relationship between the mass and the diffusion fluxes (Asano, 1976, Krishna and Standart, 1979)

$$N_i = J_{si} + \rho_{Gs} v_s \omega_{Gsi} \quad (i = 1, 2) \quad (4)$$

$$\rho_{Gs} v_s = \sum_{i=1}^2 N_i \quad (5)$$

the mass fluxes were converted into diffusion fluxes, which were plotted against the concentration driving force in Fig. 5. The proportional relationship between the diffusion fluxes and their concentration driving forces was observed. An assumption that the

Fig. 6 Vapor phase diffusion fluxes for nitrogen-oxygen and argon-oxygen systems

mass fluxes are proportional to their concentration driving forces has been used implicitly for correlation of mass transfer data. However, these results indicate that this assumption does not hold for the binary cryogenic distillation of the nitrogen-oxygen and argon-oxygen systems. Ito and Asano (1982) have already pointed out this for distillation of methanol-water system in the laminar flow.

2.3 Dimensionless diffusion fluxes

Figure 6 shows a correlation in terms of the dimensionless diffusion fluxes of oxygen defined by the following equation.

$$Sh_{GsO}(J_{sO}/N_O) = \frac{J_{sO}D}{\rho_{Gs} D_{Gs12} \Delta\omega_{GO}} \quad (6)$$

where $\Delta\omega_{GO}$ is the average concentration driving force. The ordinate is the dimensionless diffusion flux of oxygen, $Sh_{GsO}(J_{sO}/N_O)/Sc_{Gs}^{1/3}$. The abscissa is the vapor phase Reynolds number. Less scattering of data is observed in comparison with Fig. 3. The data points are very close to a straight line for each system. The observed diffusion fluxes in binary distillation with a wetted-wall column for the nitrogen-oxygen and argon-oxygen systems can be correlated by the following equation.

$$Sh_{GsO}(J_{sO}/N_O) = 0.0147 Re_G^{0.970} Sc_{Gs}^{1/3} \quad (7)$$

Kosuge *et al.* (1990, 1991) showed that vapor phase diffusion fluxes are affected by the convective mass

Fig. 7 Effect of heat flux through the wall on convective mass flux

Fig. 8 Comparison of observed convective mass flux with theoretical flux

fluxes caused by evaporation from liquids or partial condensation of mixed vapors. However, this effect may be negligible because the present study is carried out at large vapor Reynolds numbers and the distillation experiments are under low mass flux conditions ($\rho_{Gs}v_s/\rho_G U_G \approx 0$)*.

The exponent of the Reynolds number of 0.970 differs from 0.5 ($35 \leq Re_G \leq 350$) obtained in laminar flow by Olaño *et al.* (1995) and 0.805 ($32 \leq Re_G \leq 380$) by Kosuge *et al.* (1990). In this study the vapor phase Reynolds number range is approximately 3,000 –

* $\rho_{Gs}v_s/\rho_G U_G$ is a measure of the effect of condensation of mixed vapors or evaporation from liquids on the diffusion flux.

10,000. Therefore this may be due to the Reynolds number ranges and distillation systems.

2.4 Convective mass fluxes

For distillation of an air system, the perfect thermal insulation of the column is not practically available. This causes additional convective mass fluxes due to evaporation of liquid. Figure 7 shows the effect of the observed external heat fluxes through the column wall on the convective mass fluxes. The heat fluxes through the wall were estimated from the energy balance between the top and bottom of the column by

$$q_w = \frac{V_b(H_{Lb} - H_{Gb}) - V_t(H_{Lt} - H_{Gt})}{\pi DL} \quad (8)$$

and the convective mass fluxes, $\rho_{Gs}v_s$, were estimated from Eq. (5). The figure indicates that the convective mass fluxes moving towards the vapor phase from the interface increase linearly with increasing of the heat fluxes from the surroundings, and the convective mass fluxes are not zero even at adiabatic conditions ($q_w=0$).

This trend is in good agreement with the theoretical prediction by Kosuge and Asano (1982).

$$\rho_{Gs}v_s = \frac{J_{sO}(\lambda_A - \lambda_O) - q_{Gs} - q_w}{\lambda_O \omega_{GsO} + \lambda_A \omega_{GsA}} \quad (9)$$

where q_{Gs} is the vapor phase sensible heat flux.

The reason why the convective mass fluxes show finite values under adiabatic conditions may be due to the differences in the heat of vaporization of the each components and the vapor phase sensible heat fluxes.

Figures 8 shows a comparison of the observed convective mass fluxes by Eq. (5) with the theoretical ones by Eq. (9). The vapor phase sensible heat fluxes were estimated from the following equation by assuming the diffusion and heat transfer are similar.

$$Nu_{Gs} = \frac{q_{Gs}D}{\kappa_{Gs}(T_G - T_s)} = 0.0147 Re_G^{0.970} Pr_{Gs}^{1/3} \quad (10)$$

Fairly good agreement is observed. This indicates that Eq. (9) is applicable for binary distillation under the cryogenic and larger Reynolds number range conditions.

Conclusion

An experimental approach to simultaneous heat and mass transfer in binary wetted-wall column distillation was made for the nitrogen-oxygen and oxygen-argon systems under total reflux conditions for wide ranges of turbulent flow. The following results were obtained.

1) The observed diffusion fluxes for each components in binary distillation in a wetted-wall column were found to be proportional to their concentration driving forces whereas the observed mass fluxes were not.

2) The effect of the convective mass flux on the mass flux is not negligible for cryogenic air distillation.

3) A new correlation for the vapor-phase diffusion flux is proposed which can be used for both the nitrogen-oxygen and argon-oxygen systems.

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Nomenclature

c_p	= specific heat at constant pressure	[J/(kg·K)]
D_{G12}	= binary diffusion coefficient	[m ² /s]
D	= inner diameter of wetted-wall column	[m]
H	= enthalpy	[kJ/kg]
J	= diffusion flux	[kg/(m ² ·s)]
L	= length of wetted-wall column	
N	= mass flux	[kg/(m ² ·s)]
Nu_G	= vapor phase Nusselt number ($=q_G D/\kappa_G(T_G-T_s)$)	[—]
P	= pressure	[Pa]
Pr_G	= vapor phase Prandtl number ($=c_p G \mu_G/\kappa_G$)	[—]
q_{Gs}	= vapor phase sensible heat flux	[kW/m ²]
q_w	= heat flux into or out of column through the wall	[kW/m ²]
Re_G	= vapor phase Reynolds number ($=VD/S\mu_G$)	[—]
S	= cross section area of wetted-wall column	[m ²]
Sc_G	= vapor phase Schmidt number ($=\mu_G/\rho_G D_{G12}$)	[—]
Sh_G	= vapor phase Sherwood number ($=ND/\rho_G D_{G12} \Delta\omega_G$)	[—]
T	= temperature	[K]
U_G	= vapor phase superficial velocity	[m/s]
V	= mass flow rate of vapor	[kg/s]
v_s	= normal component of surface velocity	[m/s]
y	= vapor phase mole fraction	[—]
$\Delta\omega$	= concentration driving force	[—]
κ	= thermal conductivity	[kW/(m·K)]
λ	= latent heat of vaporization	[kJ/kg]
μ	= viscosity	[Pa·s]
ω	= mass fraction	[—]
ρ	= density	[kg/m ³]

<Subscript>

1	= more-volatile component
2	= less-volatile component
b	= bottom
G	= vapor phase
L	= liquid phase
i	= i -th component
O	= oxygen
s	= vapor-liquid interface
t	= top

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