k_w	catalyst = reaction rate constant in terms of unit mass of catalyst	[cm/sec]
L	= longitudinal length of cylindrical pellet	[cm]
N	= number of the mixing times	[—]
N_A	= mole flux of gas A	[mol/cm ² ·sec]
R	= reaction rate in terms of unit volume of catalyst	[g-mol/cm ³ ·sec]
R_w	= reaction rate in terms of unit mass of catalyst	[g-mol/g·sec]
R_p	= radius of a spherical pellet	[cm]
r_a	= macropore radius	[cm]
r_i	= micropore radius	[cm]
T	= absolute temperature	[°K]
V	= pore volume	[cm ³ /g]
V_p	= volume of a catalyst pellet	[cm ³]
x	= conversion of reactant gas	[—]
y_A	= mole fraction of gas A	[—]
$\bar{y}_A$	= average mole fraction between the both ends of a pellet	[—]
<Greek letters>		
β	= dimensionless skin thickness defined by δ/R_p	[—]
δ	= skin thickness	[cm]
ρ	= bulk density of a catalyst	[g/cm ³]
ρ_s	= bulk density of a skin region	[g/cm ³]
ε_a	= macropore porosity	[—]
ε_i	= micropore porosity	[—]
<Subscripts>		
A	= gas A	
a	= apparent value	
j	= pore j	
o	= overall value	

<Superscripts>

D	= non-reacting condition
i	= inlet of a reactor
R	= reacting condition
s	= skin region

Literature Cited

- 1) Aris, R.: *Chem. Eng. Sci.*, **6**, 262 (1957)
- 2) Echigoya, E. and M. Iwasaki: Preprint of the 5th Symposium on Reaction Engineering, the Soc. Chem. Engrs., Japan, p. 31 (1965)
- 3) Foster, R. N. and J. B. Butt: *A. I. Ch. E. J.*, **12**, 180 (1968)
- 4) Kasaoka, S. and U. Sakata: *J. Chem. Eng. Japan*, **2**, 138 (1968)
- 5) Korneichuk, G. P., Ya. V. Zhilailo, V. A. Roiter and I. P. Garkavenko: *Zhur. Fiz. Khim.*, **29**, 1073 (1955)
- 6) Otani, S. and J. M. Smith: *J. Catalysis*, **5**, 332 (1966)
- 7) Petersen, E. E. and J. R. Balder: *J. Catalysis*, **11**, 195, 202 (1968)
- 8) Raja Rao, M. and J. M. Smith: *A. I. Ch. E. J.*, **10**, 293 (1964)
- 9) Satterfield, C. N. and P. J. Cadle: *Ind. Eng. Chem., Process Design & Devel.*, **7**, 256 (1968)
- 10) Thiele, E. W.: *Ind. Eng. Chem.*, **31**, 916 (1939)
- 11) Wakao, N. and J. M. Smith: *Chem. Eng. Sci.*, **17**, 825 (1962)
- 12) Wakao, N. and T. Funaki: *Kagaku Kōgaku*, **31**, 485 (1967)
- 13) Wakao, N., H. Kimura, and M. Shibata: *J. Chem. Eng. Japan*, **2**, 51 (1969)
- 14) Wakao, N. and J. M. Smith: *Ind. Eng. Chem., Fundamentals*, **3**, 123 (1964)
- 15) Weisz, P. B. and A. B. Schwartz: *J. Catalysis*, **1**, 399 (1962)
- 16) Wicke, E. and R. Kallenbach: *Kolloid Z.*, **97**, 135 (1941)

OPERATING RANGE OF FALLING FILM COLUMN IN VACUUM DISTILLATION*

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It is pointed out that both the sonic velocity limit at the top (SVL) and the top pressure limit (TPL) should be considered as upper limits of vapor flow rate in a falling film column under vacuum distillation. These limits are represented in dimensionless forms and graphically, based on pressure drop equations involving a compressibility effect. Discussions are made also on the vapor Reynolds numbers corresponding to flooding and to the minimum wetting rate of reflux, and the effective operating range is illustrated.

1. Introduction

The falling film column is said to be applicable to vacuum distillation because of its low pressure drop and therefore its high allowable vapor load, but the operating limits are left uncertain due to insufficient

experimental and theoretical investigation.

The purpose of this paper is to predict how these limits vary with the operating pressure throughout a range from atmospheric to vacuum, possibly in a generalized manner.

2. Sonic Velocity Limit at the Column Top (SVL)

The upper limit of vapor load in a falling film column should be controlled by flooding if the oper-

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ating pressure is atmospheric, but under vacuum a different phenomenon arises. Under a constant bottom pressure p_1 to increase the vapor throughput, the top pressure p_2 (see **Fig. 1**) must be lowered, but after p_2 reaches a certain level it is impossible to lower p_2 further and a maximum vapor throughput is obtained depending on this value of p_2 , even if the pressure at the overhead condenser or the vacuum generator is brought to a still lower value. At this time the vapor velocity at the column top becomes comparable to the sonic velocity. Hence this limit may be called the sonic velocity limit at the column top (SVL).

3. Column Top Pressure Limit (TPL)

When the ratio of the column height to diameter is large, p_2 corresponding to SVL becomes very small compared with p_1 . In such circumstances, a minimum p_2/p_1 value will be proposed as another limit of p_2 , because extra conditions of higher vacuum are required for the equipment and the vacuum generating system if p_2 is too small compared with p_1 . This limit may be called the column top pressure limit (TPL).

4. Pressure Drop Equations

It is evident from the foregoing discussion that the pressure drop equation must be one applicable to a high velocity compressible flow.

In a continuum flow region, including both turbulent and laminar flows, a macroscopic differential momentum balance for gas flowing in a circular tube can be written as¹⁾

$$\tau_w \pi D \cdot dl = -d \left[\frac{\bar{u}^2}{u} \left(\frac{\pi D^2}{4} G \right) + \frac{\pi D^2}{4} p \right] \quad (1)$$

in which $\bar{u}^2/u$ can be approximated by $\bar{u}$ for turbulent flow while it becomes $(4/3)\bar{u}$ for a parabolic velocity distribution. Inserting $\bar{u} = G/\rho_G$, $\tau_w = f \rho_G \bar{u}^2/2$ and $\rho_G = pM/RT$, and integrating under an isothermal condition and accordingly that $f = \text{constant}$, we obtain

$$2fG^2 \frac{l}{D} + \beta \cdot G^2 \ln \left(\frac{p_1}{p_2} \right) + \frac{M}{2RT} (p_2^2 - p_1^2) = 0 \quad (2)$$

in which β is unity and $4/3$ respectively for turbulent and laminar flows. This is only a combined equation between those of Dodge (turbulent)²⁾ and Schwartzberg *et al.* (laminar).¹³⁾

In distillation the vapor flow may undergo nearly an adiabatic process rather than isothermal although mass transfer takes place between the vapor and falling liquid. If Eq.(1) is to be integrated under the adiabatic condition of $p/\rho_G^\gamma = \text{constant}$, the factor f must be considered a variable and the integrated result becomes considerably complex. Some reasons why the authors adopted the isothermal condition are as follows. (1)

Fig. 1 Illustrative diagram

An equation as simple as possible is desired for the following generalized discussion. (2) The temperature variation in a distillation column is probably not so significant in the absolute temperature scale. (3) Most of the materials treated in vacuum distillation are polyatomic, and then it is expected that $\gamma = c_p/c_v$ will be nearly unity.

Next in the slip, transition and molecular flow regions, Knudsen's semi-empirical equation may be applied. The original equation⁹⁾ can be rewritten as

$$\frac{\pi}{4} D^2 G = \left[\frac{\pi}{128} \frac{1}{\mu_G} \frac{D^4}{l} \rho_{Gav} + \frac{1}{6} \sqrt{2\pi} \sqrt{\frac{M}{RT}} \right. \\ \left. \times \frac{D^3}{l} \frac{1 + \frac{\rho_{Gav}}{\mu_G} \sqrt{\frac{RT}{M}} D}{1 + 1.235 \frac{\rho_{Gav}}{\mu_G} \sqrt{\frac{RT}{M}} D} \right] (p_1 - p_2) \quad (3)$$

in which ρ_{Gav} is to be evaluated at $p_{av} = (p_1 + p_2)/2$. The first term in the right side of Eq.(3) corresponds to the Poiseuille flow rate and when the pressure is reduced it becomes less important compared with the second term which is the molecular flow rate modified empirically.

This equation is correlated to experimental data obtained under conditions of long tube ($l/D \gg 1$) and of somewhat high value in p_1/p_2 . Therefore the compressibility effect may be involved in this equation.

5. Dimensionless Expression of the Pressure Drop Equations

As is well known the kinetic theory of gases shows

that the viscosity of a gas is related to the molecular mean speed $\bar{c} (= \sqrt{8RT/\pi M})$ and the mean free path λ as

$$\mu_G = (1/2)\rho_G \bar{c} \lambda \quad (4)$$

Using this relation we obtain

$$Re_G = \frac{D \bar{u} \rho_G}{\mu_G} = \sqrt{\frac{\pi}{2}} \frac{Ma}{Kn} \quad (5)$$

where $Ma (= \bar{u}/U)$ is the isothermal Mach number and $Kn (= \lambda/D)$ is the Knudsen number which is a measure of the rarefaction. Eqs.(4) and (5) will be used to rearrange the pressure drop equations to dimensionless expressions.

5.1 Turbulent region

For simplicity the friction factor f is substituted from the Blasius formula of $0.0791 Re_G^{-1/4}$, then Eq.(2) becomes

$$\left(\frac{p_1}{p_2}\right)^2 - 1 = 0.3164 Ma_2^2 Re_G^{-1/4} \frac{l}{D} + 2 Ma_2^2 \ln\left(\frac{p_1}{p_2}\right) \quad (6)$$

5.2 Laminar region

Substituting $f = 16/Re_G$ in Eq.(2) we obtain

$$\left(\frac{p_1}{p_2}\right)^2 - 1 = 8 \sqrt{\frac{2}{\pi}} Kn_2 Ma_2 \times \left[8 \frac{l}{D} + \frac{Re_G}{3} \ln\left(\frac{p_1}{p_2}\right) \right] \quad (7)$$

5.3 Slip to molecular flow region

Eq.(3) is rewritten as

$$\left(\frac{p_1}{p_2}\right)^2 - 1 = 64 \sqrt{\frac{2}{\pi}} Kn_2 Ma_2 \frac{l}{D} \left[1 + \frac{256}{3\pi} \frac{Kn_2}{\frac{p_1}{p_2} + 1} \frac{Kn_2 + \sqrt{\frac{\pi}{8}} \left(\frac{p_1}{p_2} + 1\right)}{Kn_2 + 1.235 \sqrt{\frac{\pi}{8}} \left(\frac{p_1}{p_2} + 1\right)} \right] \quad (8)$$

In these equations Ma_2 and Kn_2 are to be evaluated at the pressure of p_2 . Eqs.(6) through (8) were calculated and the result is shown in **Fig. 2**. Ranges assigned to each equation are as follows.

Eq.(6): $Re_G > 3000$

Eq.(7): $Re_G < 2000$ and $Kn_2 < 10^{-2}$

Eq.(8): $Kn_2 > 10^{-2}$

Values calculated from Eqs.(7) and (8) could be connected satisfactorily at the junctions. The quantity $[(p_1 - p_2)/p_2]/(l/D)$ is determined independently of l/D for low Ma_2 or high Kn_2 , but as Ma_2 increases or Kn_2 decreases the curves branch off following various l/D values. Thus to avoid complication only two cases in l/D are shown in **Fig. 2**. While in this chart the curves drawn with Re_G are extended over the whole range of Kn_2 . At higher Kn_2 , of course, the viscosity in Re_G should be defined in the unbounded space and Re_G may be considered merely as the parameter $\sqrt{\pi/2} Ma_2/Kn_2$ (see Eq.(5)) or physically as a measure

of the reflux flow rate per unit width (see Eq.(13)). It should be noted that the original or physical concept of the Reynolds number is lost in the transition and molecular flow regions.

The sonic velocity limit (SVL) can be considered to be the curve of $Ma_2 = 1$. The top pressure limit (TPL) may be illustrated, for example, as follows. When l/D is 100 and the pressure drop limitation is given so that $\Delta p/p_2 < 2$ ($p_1/p_2 < 3$), it becomes clear that $(\Delta p/p_2)/(l/D) < 2 \times 10^{-2}$, and therefore we may find that TPL controls when Kn_2 is greater than about 1×10^{-3} referring to **Fig. 2** (see also **Fig. 3**).

6. Flooding Limitation

A reliable correlation on the flooding in a wetted wall column was given by Kamei *et al.*⁷⁾, which was reexamined afterwards by Iijima *et al.*⁸⁾ and Fujita⁴⁾. Although these experiments were performed under conditions of atmospheric pressure and turbulent flow of gases, the correlation may be applicable still at reduced pressures if the gas flow is only continuum and turbulent. By substituting a definition of the reflux ratio, $r = L/(G - L)$, the original flooding equation can be rewritten as

$$Re_G = 198^{0.816} \left(\frac{r+1}{r}\right)^{0.184} \left(\frac{\mu_L}{\mu_G}\right)^{0.42} \left(\frac{\rho_G}{\rho_L}\right)^{0.106} \times \left(\frac{D^5 \rho_L^3 g^2}{\sigma_L \mu_L^2}\right)^{0.188} \quad (9)$$

If one desires to superimpose this Re_G upon **Fig. 2**, the following rearrangement will be available. Considering that the exponent of ρ_G , 0.106, is small compared with unity, and then putting $\rho_G^{0.106} \div \rho_{G2}^{0.106} = (2\mu_G/\bar{c}\lambda_2)^{0.106}$, we can rewrite Eq.(9) as

$$Re_G = Z D^{0.834} Kn_2^{-0.106} \quad (10)$$

where

$$Z = 198^{0.816} 2^{0.106} \left(\frac{r+1}{r}\right)^{0.184} \rho_L^{0.458} \mu_L^{0.044} \times \sigma_L^{-0.188} \bar{c}^{-0.106} \mu_G^{-0.314} g^{0.376} \quad (11)$$

Here Z does not depend directly upon the operating pressure, and furthermore its dependence on various materials treated or on variation of the reflux ratio is relatively slight. This range in Z is shown in **Table 1** along with roughly assumed ranges of the variables. For example, if we take Z of 3×10^3 and D of 2 cm, a flooding Reynolds number of $5.346 \times 10^3 \times Kn_2^{-0.106}$ is obtained from Eq.(10) and this is represented in **Fig. 3**. The asymptote of the flooding line for small Kn_2 can be derived from Eq.(6); the result is

$$\left(\frac{p_1 - p_2}{p_2} \right) / \left(\frac{l}{D}\right)_{\text{Flooding, Asymptote}} = 8.53 \times 10^{-11} Z^{7/4} D^{1.458} (10^5 Kn)^{1.814} \quad (12)$$

It should be noted that for Z in the range estimated in **Table 1** the resulting flooding Reynolds number

Fig. 2 Results calculated from Eqs. (6) through (8)

Fig. 3 Four limits based on examples described

Table 1 Rough estimation of range in Z

r	0.5– ∞	$\left(\frac{r+1}{r}\right)^{0.184}$	1–1.224
ρ_L	0.7–1.5 [g/cm ³]	$\rho_L^{0.458}$	0.894–1.204 [CGS]
μ_L	0.1–100 [cp]	$\mu_L^{0.044}$	0.738–1 [CGS]
σ_L	10–70 [dyne/cm]	$\sigma_L^{-0.188}$	0.450–0.649 [CGS]
T	300–500 [°K]		
M	20–1000 [g/g-mole]		
$\bar{c} = \sqrt{\frac{8RT}{\pi M}}$	7.98×10^3 – 7.28×10^4 [cm/sec]	$\bar{c}^{-0.106}$	0.306–0.396 [CGS]
μ_G	0.01–0.02 [cp]	$\mu_G^{-0.314}$	14.50–18.03 [CGS]
Z			$(1.32\text{--}6.84) \times 10^3$ [l/cm ^{0.834}]

exceeds 3000, therefore the flow is turbulent when the tube diameter is greater than 1 cm.

7. Lower Limit of Vapor Flow Rate Based on the Minimum Wetting Rate of Reflux

If the flow rate of reflux is insufficient to wet the entire wall surface, operation will become disadvantageous because the dry part does not contribute to mass transfer but increases the pressure drop. If the minimum liquid flow rate, $\Gamma_{\min}$, required to completely wet the wall surface is known, the lower limit of vapor flow rate corresponding to $\Gamma_{\min}$ is written as

$$\Gamma_{\min} = \frac{1}{\pi D} \frac{\pi D^2}{4} G \frac{r}{r+1} = \frac{D}{4} G \frac{r}{r+1}$$

or

$$Re_G = \frac{r+1}{r} \frac{4\Gamma_{\min}}{\mu_G} \quad (13)$$

Hartley *et al.*⁵⁾ and Ponter *et al.*¹¹⁾ investigated $\Gamma_{\min}$ both theoretically and experimentally, but the results suggest that it is difficult at present to estimate $\Gamma_{\min}$ by a generalized method applicable to various liquids and wall materials.

Furthermore in distillation, the surface tension of the falling liquid varies as it flows down because of both its composition and temperature variations. Also as pointed out by Zuiderweg *et al.*¹⁴⁾, the positive system in which the surface tension increases down the column will result in desirable wetting but the negative system will act in the wrong way. Thus for negative systems it seems that various efforts should be made so that $\Gamma_{\min}$ might be lowered, for example, by the use of surface active agents³⁾ or distributing devices.

While for a positive system there must be a value of $\Gamma_{\min}$ even if the system exhibits good wetting behavior. This value seems to fall out about 0.005 g/cm-sec in preferably wetting systems according to available data^{10,12)} and the authors' experience on vacuum distillation. If this value of $\Gamma_{\min} = 0.005$ g/cm-sec and the fact that the viscosity of most of gases is in the range of 0.01–0.02 cp are substituted in Eq.(13), the condition of $Re_G = 100$ –200 is required for complete wetting even under total reflux. This criterion is shown also in Fig. 3.

8. Discussion

The foregoing criteria for the operating limitations of the falling film column under vacuum distillation are summarized in Fig. 3 based on the examples described individually. The region enclosed by the four limiting lines is considered applicable to operate effectively. In this example, it can be well explained that the upper limit of the vapor throughput is controlled by flooding at higher pressures (at lower Knudsen numbers), and as the pressure is reduced SVL or TPL becomes controlling.

Fig. 3 indicates also that the vapor flow must be laminar at pressures below a value corresponding to the intersection between the lines of $Re_G = 2000$ and of the upper controlling limit. It has been often stated with only a qualitative explanation that the vapor flow must be laminar at very low pressures⁸⁾. The above observation apparently provides important quantitative support for this statement.

Next the lower limit of the vapor throughput controlled by the minimum wetting rate will be noted. If the corresponding Re_G does not reach below 100 as assessed before, Kn_2 will not exceed about 10^{-2} , and then it will not be necessary to take account of the rarefaction effect on transport phenomena in the vapor phase.

Nomenclature

$\bar{c}$	= molecular mean speed	[cm/sec]
D	= column diameter	[cm]
f	= Fanning friction factor	[—]
G	= mass velocity of vapor	[g/cm ² -sec]
g	= acceleration due to gravity	[cm/sec ²]
Kn	= Knudsen number = λ/D	[—]
L	= mass velocity of reflux = mass flow rate per unit area of column	[g/cm ² -sec]
l	= column height	[cm]
M	= molecular weight of vapor	[g/g-mole]
Ma	= isothermal Mach number	[—]
p	= pressure	[dyne/cm ²]
R	= gas constant = 8.314×10^7	[g·cm ² /sec ² ·g-mole·°K]
Re_G	= Reynolds number = $D\bar{u}_G/\mu_G$	[—]
r	= reflux ratio = $L/(G-L)$	[—]
T	= absolute temperature	[°K]
U	= isothermal sonic velocity = $\sqrt{RT/M}$	[cm/sec]
$\bar{u}$	= average velocity of vapor for cross section	[cm/sec]
$\bar{u}^2$	= mean square velocity of vapor for cross section	[cm ² /sec ²]
Z	= defined in Eq.(11)	[l/cm ^{0.834}]

β	= defined in Eq.(2)	[—]
$\Gamma_{\min}$	= minimum wetting rate of falling liquid per unit width of wall	[g/cm-sec]
λ	= molecular mean free path	[cm]
μ	= viscosity	[g/cm-sec]
ρ	= density	[g/cm ³]
σ_L	= surface tension of liquid	[dyne/cm]
<Subscripts>		
G	= for vapor	
L	= for liquid	
1	= at the bottom of column	
2	= at the top of column	
av	= at pressure $p_{av} = (p_1 + p_2)/2$	

Literature Cited

- 1) Bird, R. B., W. E. Stewart and E. N. Lightfoot: "Transport Phenomena", p. 211, Wiley, New York (1960)
- 2) Dodge, B. F.: "Chemical Engineering Thermodynamics"

- p. 350, McGraw-Hill, New York (1944)
- 3) Francis, R. C. and J. C. Berg: *Chem. Eng. Sci.*, **22**, 685 (1967)
- 4) Fujita, S.: *Kagaku Kōgaku*, **30**, 179 (1966)
- 5) Hartley, D. E. and W. Murgatroyd: *Int. J. Heat & Mass Transfer*, **7**, 1003 (1964)
- 6) Iijima, T. and T. Kuzuoka: *Kagaku Kōgaku*, **31**, 1240 (1967)
- 7) Kamei, S., J. Oishi and T. Okane: *Kagaku Kōgaku*, **18**, 364 (1954)
- 8) King, R. W.: *Brit. Chem. Eng.*, **12**, 722 (1967)
- 9) Knudsen, M.: *Ann. Phys.*, **28**, 75 (1909)
- 10) Norman, W. S. and D. T. Binns: *Trans. Instn. Chem. Engrs.*, **38**, 294 (1960)
- 11) Ponter, A. B., G. A. Davies, T. K. Ross and P. G. Thornley: *Int. J. Heat & Mass Transfer*, **10**, 349 (1967)
- 12) Ponter, A. B., G. A. Davies, W. Beaton and T. K. Ross: *Trans. Instn. Chem. Engrs.*, **45**, T345 (1967)
- 13) Schwartzberg, H. G. and M. Gurevich: *A. I. Ch. E. Journal*, **16**, 762 (1970)
- 14) Zuiderweg, F. J. and A. Harmens: *Chem. Eng. Sci.*, **9**, 89 (1958)

DISTILLATION CALCULATION BY THE MODIFIED PERTURBATION METHOD*

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An unique perturbation method for the distillation calculation of a non-ideal system was proposed by Acrivos and Amundson. This method, however, is limited only to the first-order perturbation and gives an approximate solution, for the equation with the second and further perturbed terms is too complicated to use for practical purposes. To improve this point the Double Perturbation Method is presented here. Although the equations used in the presented method are obtained by the same reasoning as the above authors, this method, whose tiresome procedures can be overcome by computer, gives the strict solution.

1. Introduction

An interesting perturbation method for the distillation calculation was proposed by Acrivos and Amundson^{1,2)}. In their procedure, at first a non-perturbed distribution profile is obtained and next the first-order perturbed terms are calculated. The non-perturbed distribution profile is corrected by these first-order perturbed terms. From a mathematical viewpoint, this method is very interesting and moreover implies further application. The solution, however, sometimes remains an approximate one, for the second-order term and further terms are truncated. If these

terms were considered, from the practical computational stand-point, the procedures would be too complicated to carry out the calculation as Acrivos and Amundson described it in their paper. The equations used in the following method are derived by the same reasoning as the above authors.

The equations concerning an enriching section of a column have been presented by them. But for a stripping section only the final equations of the non-perturbed case are presented in their work.

The strict solution can be obtained by repeated application of a multi-usage of the first-order perturbation, the detailed explanation of which will be described in a later section.

2. The Basic Equations for the Stripping Section of a Rectification Column

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