LETTERS IN HEAT AND MASS TRANSFER
Vol. 3, pp. 163 - 172, 1976

Pergamon Press
Printed in the United States

AN ACKERMANN-COLBURN AND DREW TYPE ANALYSIS FOR CONDENSATION OF MULTICOMPONENT MIXTURES

R. Krishna, C.B. Panchal, D.R. Webb and I. Coward

Department of Chemical Engineering
University of Manchester Institute of Science and Technology
Sackville Street, Manchester M60 1QD, England

(Communicated by D.B. Spalding)

ABSTRACT

This paper considers design procedures for condensation of multicomponent mixtures. Using essentially a 'film' model, the rate relations for heat and mass transfer in the vapour and liquid phases are formulated and combined with differential material and energy balances to yield design equations. The mass transfer analysis includes the possibility of diffusional interactions.

A sample design problem for condensation of a 6-component mixture is considered and the results with the complete analysis are compared with three other simpler approaches: (i) a model based on assuming negligible diffusional interactions and using uncoupled rate relations, (ii) the procedure suggested by Bell and Ghaly in which the mass transfer resistance is ignored but compensated for by overestimation of the heat transfer resistance and (iii) an equilibrium design procedure in which the vapour and liquid phases are assumed to be in equilibrium.

The results show that neglect of diffusional interactions might lead to severe underdesign. The Bell and Ghaly method gives a surprisingly good estimate of the condenser area required.

Introduction

Design of heat exchangers to partially or totally condense an $\underline{n}$-component vapour mixture, often in the presence of an inert gas, is frequently necessary in the process industries. The process of condensation involves simultaneous transfer of mass and energy between the condensing vapour and liquid streams. Established design procedures for condensation of binary vapour mixtures follow the classic transfer analyses of Ackermann [1] and Colburn and Drew [2]. Published extensions to the general *n*-component case (e.g. Schrodt [3]) assume negligible diffusional interactions in the vapour and use uncoupled mass transfer rate relations. These non-interacting transfer models may be considered adequate for very lean vapour mixtures condensing in the presence of a large excess of non-condensable gas. The design procedure suggested by Bell and Ghaly [4] ignores the mass transfer aspect of the problem and compensates by overestimating the heat transfer resistance.

It is our object here to consider the condensation of *n-1* vapour species in the presence of a stagnant *n*th component. Proper account is taken of the possibilities of diffusional interactions between the condensing species. The analysis of the mass and energy transfer processes in the vapour and condensate liquid phases is based on 'film' model and represents essentially an extension of the treatments of Ackermann and Colburn and Drew. For definiteness we consider condensation to take place inside a single vertical tube with the vapour and liquid streams in co-current flow. The coolant is assumed to flow counter-current to the condensate, in the annular section outside the tube. Other geometries and flow configurations can be easily accommodated in the ensuing analysis with minor changes only.

Mass and Energy Transfer Analysis

The differential molar material balance for each of the *n-1* condensing species in the vapour phase takes the form

$$\frac{dG_i}{dZ} = - N_i^y \, a \, A \qquad i = 1,2,\ldots n-1 \qquad (1)$$

where G_i is the molar flow rate of the species *i* and N_i^y is the molar flux of species *i* in the vapour phase; Z represents the distance from the top of the condenser tube.

The *n*th species is considered to be stagnant or inert and therefore

$$N_n^y = 0 \qquad (2)$$

which means that the inert gas flow rate is constant or

$$\frac{dG_n}{dZ} = - N_n^y \, a \, A = 0 \qquad (3)$$

The molar rates of transfer of the condensing species may be split up into diffusive and convective contributions as

$$N_i^y = J_{ib}^y + y_{ib} \, N_t^y, \qquad i = 1,2,\ldots n \qquad (4)$$

where N_t^y is the mixture molar flux and given by

$$N_t^y = \sum_{k=1}^{n} N_i^y \qquad (5)$$

Taking account of diffusional interactions in the vapour phase, the constitutive relations for mass transfer may be written as

$$J^y_{ib} = \sum_{k=1}^{n-1} k^\bullet_{ybij}(y_{jb} - y_{jI}), \qquad i = 1,2,\ldots n-1 \qquad (6)$$

where the $k^\bullet_{ybij}$ represent the elements of the matrix of vapour phase mass transfer coefficients, $[k^\bullet_{yb}]$, of dimension $\underline{n-1}\times\underline{n-1}$. The cross coefficients, $k^\bullet_{ybij}$ $(i\neq j)$ portray the diffusional interactions or coupling phenomena.

There are basically two procedures in the literature for estimating the elements of the matrix $[k^\bullet_{yb}]$ from information on the transport parameters of the constituent <u>binary</u> pairs. These are (i) based on the linearized theory of multicomponent mass transfer, developed independently by Toor [5] and Stewart and Prober [6] and (ii) the recently developed multicomponent 'film' model based on an exact matrix method of solution to the Maxwell-Stefan equations [7]. The procedure for calculating $[k^\bullet_{yb}]$ using these two approaches is summarized below.

(i) Calculation of $[k^\bullet_{yb}]$ from Toor-Stewart and Prober approach

STEP I Calculate the elements of the matrix of diffusion coefficients in the vapour phase, $[D]$, using average vapour compositions between bulk (y_b) and interface (y_I) at any given position, from

$$[D] = [A]^{-1} \qquad (7)$$

where the elements of $[A]$ are given by

$$A_{ii} = \frac{y_i}{\mathcal{D}_{in}} + \sum_{\substack{k=1\\k\neq i}}^{n} \frac{y_k}{\mathcal{D}_{ik}}, \qquad i = 1,2,\ldots n-1 \qquad (8)$$

$$A_{ij} = -\, y_i(1/\mathcal{D}_{ij} - 1/\mathcal{D}_{in}), \qquad \begin{matrix} i,j = 1,2,\ldots n-1 \\ i\neq j \end{matrix} \qquad (9)$$

where the vapour phase diffusivities of the binary pairs in the mixture, $\mathcal{D}_{ik}$, can be estimated from the kinetic theory or from semi-empirical correlations [8]. The linearized theory assumes that the elements of the matrix $[D]$ are constant along the diffusion path and therefore average compositions y_i must be used in equations (8) and (9). Once the elements of $[A]$ are obtained, the matrix $[D]$ can be calculated from (7). The eigenvalues $\hat{D}_i$ of $[D]$ can now be obtained using appropriate numerical procedures.

STEP II Pseudo-zero flux mass transfer coefficients $\hat{k}_i$ are now calculated from standard correlations say of the j factor type using the <u>i</u>th eigenvalue $\hat{D}_i$ in place of the binary diffusivity $\mathcal{D}_{ik}$.

STEP III These zero flux coefficients are corrected for finite rates of transfer by

$$\hat{k}^{\bullet}_{i} = \hat{k}_{i}\,\frac{\psi_{i}}{\exp\psi_{i} - 1}\ ;\ \text{with}\ \psi_{i} = \frac{N^{y}_{t}}{\hat{k}_{i}}, \qquad i = 1,2,\ldots n-1 \qquad (10)$$

STEP IV Estimate the matrix $[k^{\bullet}_{yb}]$ from

$$[k^{\bullet}_{yb}] = [P]\ulcorner \hat{k}^{\bullet} \lrcorner [P]^{-1} \qquad (11)$$

where $[P]$ is the modal matrix of $[D]$.

(ii) <u>Calculation of $[k^{\bullet}_{yb}]$ using multicomponent film model of Krishna and Standart</u> [7]

STEP I Calculate the elements of the matrix of zero flux mass transfer coefficients $[k_{yb}]$ from

$$[k_{yb}] = [B_{b}]^{-1} \qquad (12)$$

where the elements of $[B_{b}]$ are obtained from

$$B_{bii} = \frac{y_{ib}}{\textit{k}_{in}} + \sum_{\substack{k=1\\k\neq i}}^{n} \frac{y_{kb}}{\textit{k}_{ik}}, \qquad i = 1,2,\ldots n-1 \qquad (13)$$

$$B_{bij} = -\,y_{ib}(1/\textit{k}_{ij} - 1/\textit{k}_{in}), \qquad i,j = 1,2,\ldots n-1 \quad i\neq j \qquad (14)$$

The zero flux mass transfer coefficients of the binary pairs $\textit{k}_{ik}$ are estimated from standard binary mass transfer correlations using estimated values of $\mathcal{D}_{ik}$.

STEP II From the knowledge of the transfer rates, N^{y}_{i}, obtain the matrix of correction factors

$$[\Xi] = [\Phi]\{\exp[\Phi] - \ulcorner I \lrcorner\}^{-1} \qquad (15)$$

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

$$\Phi_{ii} = \frac{N^{y}_{i}}{\textit{k}_{in}} + \sum_{\substack{k=1\\k\neq i}}^{n} \frac{N^{y}_{k}}{\textit{k}_{ik}}, \qquad i = 1,2,\ldots n-1 \qquad (16)$$

$$\Phi_{ij} = -\,N^{y}_{i}\,(1/\textit{k}_{ij} - 1/\textit{k}_{in}), \qquad i,j = 1,2,\ldots n-1 \quad i\neq j \qquad (17)$$

The matrix of correction factors can be evaluated by using Sylvester's expansion theorem [9].

STEP III The elements of the matrix $[k^{\bullet}_{yb}]$ are then obtained from

$$[k^{\bullet}_{yb}] = [k_{yb}][\Xi] \qquad (18)$$

Once the elements $k^{\bullet}_{ybij}$ have been estimated by either of the two procedures outlined above, we may calculate the diffusion fluxes from (6) and the total fluxes N^y_i are obtained in view of equations (2) and (4) as

$$N^y_i = \sum_{k=1}^{n-1} (\delta_{ik} + y_{ib}/y_{nb})\, J^y_{kb}, \qquad i = 1,2,\ldots n-1 \qquad (19)$$

Since the evaluation of the finite flux coefficients $k^{\bullet}_{ybij}$ requires a prior knowledge of these total fluxes, N^y_i, it is clear that a trial and error procedure is involved in the calculations at every position along the condenser. Stable convergence is assured if the initial calculations are carried out assuming that the finite flux coefficients equals the zero flux coefficients.

Turning now to the analysis of the liquid phase transport, we have the differential molar material balance for the $\underline{n-1}$ species in the liquid condensate as

$$\frac{dL_i}{dZ} = N^x_i\, a\, A, \qquad i = 1,2,\ldots n-1 \qquad (20)$$

with the interfacial total molar flux in the liquid phase given by

$$N^x_i = J^x_{ib} + x_{ib}\, N^x_t = J^x_{iI} + x_{iI}\, N^x_t, \qquad i = 1,2,\ldots n-1 \qquad (21)$$

where the diffusion fluxes may be related to the composition driving forces using relations analogous to (6) with a matrix of mass transfer coefficients of dimension $\underline{n-2}\times\underline{n-2}$. Multicomponent diffusion coefficient data are relatively scarce and an estimation of such a matrix of coefficients cannot be carried out. When the vapour phase contains a non-condensable gas, as was assumed in the current analysis, the mass transfer process is essentially dictated by the vapour phase behaviour and the inability to estimate liquid phase mass transfer coefficients is not serious in most cases. In order to confirm this conclusion, the calculations reported for the design problem below were carried out with two extreme assumptions:

(i) a completely mixed condensate film, equivalent to infinite mass transfer coefficients in the liquid phase, whence

$$x_{ib} = x_{iI}, \qquad i = 1,2,\ldots n-1 \qquad (22)$$

(ii) a completely unmixed condensate film, equivalent to zero values for the mass transfer coefficients in the liquid phase, whence

$$J^x_{iI} = 0; \quad x_{iI} = N^x_i/N^x_t, \qquad i = 1,2,\ldots n-1 \qquad (23)$$

The calculations for the design problem considered showed very little difference in the final results with these extremes for liquid phase behaviour and therefore it may be concluded that the liquid phase mass transfer resistance is not important. The results for the completely unmixed film are only reported for the design problem below.

The interface conditions must be such that at every position along the condenser, the continuity of interfacial molar fluxes must be satisfied, i.e.

$$N_i^y = N_i^x = N_i, \qquad i = 1,2,\ldots n-1 \qquad (24)$$

The variation of the temperature of the vapour-gas mixture is given by a differential energy balance as

$$G_t C_p^y \frac{dT_b}{dZ} = -q^y a A = h_y^\bullet (T_b - T_I) a A \qquad (25)$$

where $h_y^\bullet$ is the heat transfer coefficient in the vapour, corrected for finite mass transfer rates by the Ackermann-Colburn and Drew theory. The zero flux coefficient h_y may be estimated from standard j-factor correlations.

The interface conditions (T_I, x_{iI}, y_{iI}) must also satisfy the condition of continuity of energy fluxes:

$$E^y = q^y + \sum_{k=1}^{n} \overline{H}_i^y N_i = q^x + \sum_{k=1}^{n} \overline{H}_i^x N_i = E^x \qquad (26)$$

or

$$q^x = q^y + \sum_{k=1}^{n} (\overline{H}_i - \overline{H}_i^x) N_i \qquad (27)$$

If we neglect condensate subcooling the conductive heat flux q^x may be written as

$$q^x = q^w = h_o (T_I - T_c) \qquad (28)$$

where the coefficient h_o accounts the heat transfer resistance for the condensed liquid film, wall and coolant. The variation of the coolant temperature T_c is given by

$$L_c C_{pc} \frac{dT_c}{dZ} = -q^w a A = h_o (T_I - T_c) \qquad (29)$$

If we assume that we have thermodynamic equilibrium between the vapour and liquid phase at the interface and if constant pressure operation is assumed, there will be $\underline{n-1}$ unknown interfacial parameters from T_I, x_{iI} to determine. A convenient calculation procedure is to use multi-dimensional Newton-Raphson iteration to converge on the values of the unknown parameters such that the interfacial relations (24) and (27) are satisfied. Condenser design calculations may be carried out using a finite difference approximation to the differential material and energy balance relations.

Design Exercise and Discussion

The general design procedure outlined above was used to find the area required to condense 50% of a mixture of hydrocarbon vapours in the presence of 'inert' hydrogen gas. The details of the single tube condenser and inlet operating conditions can be found in Table 1. The physical, thermodynamic and equilibrium data for the hydrocarbon vapour and liquid phases were taken from literature sources or estimated using critical properties and an equation of state. The results with the two different estimation procedures for $[k^{\bullet}_{yb}]$ are given in Table 2 which gives the outlet vapour compositions, vapour temperature and the area required for condensation. Both the multicomponent film model and the linearized theory approaches give results which are not significantly different from each other.

To study the effect of diffusional interactions on the system behaviour, a naive, non-interacting type, mass transfer model assuming uncoupled rate relations of the form

$$J^{y}_{ib} = k_{i,eff}(y_{ib} - y_{iI}), \qquad i = 1,2,\ldots n-1 \qquad (30)$$

was also used in the design exercise. The effective mass transfer coefficient was obtained assuming that each species behaves as though it were diffusing through stagnant hydrogen. The results with this naive approach show that neglect of vapour phase diffusional interactions leads to severe underdesign. The conclusion to be drawn here is that for multicomponent systems, one may not use uncoupled rate relations of the form (30).

The Bell and Ghaly method was also used in this design exercise. In this method the mass transfer resistances are completely ignored and 'compensated' by an overestimation of the heat transfer resistance. This method gives only a small overdesign as compared to the proper 'interactive' mass transfer analysis. The result must be viewed as fortuitous because the Bell and Ghaly procedure is not based on any sound simultaneous heat and mass transfer theory.

The assumption that the vapour and liquid phases are in thermodynamic equilibrium gives the minimum amount of condensation area required, 0.041 m^2.

From a practical point of view, the model developed in this work needs to be tested with experimental data. Once the simultaneous heat and mass transfer model has been validated, various approximate procedures can be worked out for use in industrial heat exchanger design.

TABLE 1

Summary of Condenser Tube Data and Inlet Conditions

Geometry: single vertical tube (diameter, d = 0.0254 m) with condensation taking place inside the tube; cooling water flowing in annular section

Flow Directions: hydrocarbon mixture flowing down the tube, co-current to condensate; cooling water flowing up the annulus, counter-current to the flow of condensate liquid

Entering Vapour Temperature: 345.4 K

Pressure of Vapour at Inlet: 1.0135 bar (assumed constant throughout tube)

Coolant Water Flow Rate: 0.04376 kg/s

Coolant Temperature at Top of Tube: 283.15 K

Heat Transfer Coefficient: h_o = 1700 W/(m^2)(K)

Vapour Phase Heat and Mass Transfer Coefficients: calculated from analogy

$$j_D = \frac{k_y A}{G_t}(Sc)^{2/3} = j_H = \frac{h_y A}{G_t C_p}(Pr)^{2/3} = 0.023\ (Re)^{-0.17}$$

Component Molar Flow Rates and Mole Fractions at Inlet:

propane (1)	$G_1 = 1.05\times10^{-5}$ kmol/s;	$y_1 = 0.150$
n-butane (2)	$G_2 = 0.63\times10^{-5}$ kmol/s;	$y_2 = 0.090$
n-hexane (3)	$G_3 = 1.26\times10^{-5}$ kmol/s;	$y_3 = 0.180$
n-heptane (4)	$G_4 = 0.42\times10^{-5}$ kmol/s;	$y_4 = 0.060$
n-octane (5)	$G_5 = 0.84\times10^{-5}$ kmol/s	$y_5 = 0.120$
hydrogen (6)	$G_6 = 2.80\times10^{-5}$ kmol/s	$y_6 = 0.400$

TABLE 2

Comparison of Outlet Vapour Compositions and Tube Areas Required for Condensing 50% of Vapour Mixture (Components 1-5)

	y_1	y_2	y_3	y_4	y_5	y_6	T	Area, m^2
Krishna & Standart Multicomp. Model	0.200	0.102	0.078	0.018	0.031	0.572	293.7	0.115
Linearized Theory Multicomp. Model	0.200	0.100	0.076	0.017	0.030	0.574	291.4	0.125
Effective Diffusivity Model	0.204	0.109	0.084	0.013	0.015	0.574	302.5	0.085
Bell and Ghaly Design Procedure	0.203	0.109	0.092	0.014	0.010	0.571	301.2	0.138
Equilibrium Design Procedure	0.203	0.109	0.092	0.014	0.010	0.571	301.2	0.041

Nomenclature

a	interfacial area per unit volume of tube, m^2/m^3
A	cross-sectional area of tube, m^2
$[A]$	inverted diffusion coefficients with elements given by (8),(9)
$[B_b]$	inverted mass transfer coefficients with elements as (13), (14)
C_p	molar heat capacity, J/(kmol)(K)
d	inside diameter of tube, m
$\mathcal{D}_{ik}$	vapour phase diffusivity of binary pair i-k, m^2/s
$[D]$	matrix of diffusion coefficients, m^2/s
$\mathcal{D}_{i,eff}$	effective diffusivity of species *i* in mixture, m^2/s
E	phase invariant total energy flux, W/m^2
G_i	molar flow rate of species *i* in vapour phase, kmol/s
h	heat transfer coefficient, $W/(m^2)(K)$
$\overline{H}_i$	partial molar enthalpy of species *i*, J/kmol
J_i	molar diffusion flux of species *i*, $kmol/(s)(m^2)$
k_{ik}	mass transfer coefficient of binary pair i-k, $kmol/(s)(m^2)(\Delta y)$
$[k]$	matrix of multicomponent mass transfer coefficients, $kmol/(s)(m^2)(\Delta y)$
L_i	molar flow rate of species *i* in liquid, kmol/s
N_i	total molar flux of species *i*, $kmol/(s)(m^2)$
N_t	mixture total flux, $kmol/(s)(m^2)$
q	conductive heat flux, W/m^2
Re	Reynolds number
Sc	Schmidt number
x_i	mole fraction of species *i* in liquid mixture
y_i	mole fraction of species *i* in vapour mixture
Z	length along condenser tube measured from the top

Greek Letters

δ_{ik}	Kronecker delta
$[\Xi]$	matrix of correction factors given by (15)
$[\Phi]$	matrix of dimensionless rate factors given by (16) and (17)
ψ_i	pseudo rate factor given by equation (10)

Matrix Notation

$(\ )$	column matrix of dimension *n-1*

Matrix Notation (Cont'd)

$[\ ]$	$\underline{n-1}\times\underline{n-1}$ dimensional square matrix
$[\ ]^{-1}$	$\underline{n-1}\times\underline{n-1}$ dimensional inverted matrix
$\ulcorner\ \lrcorner$	diagonal matrix with $\underline{n-1}$ non-zero elements
$\ulcorner I \lrcorner$	identity matrix with elements δ_{ik}

Subscripts

b	bulk fluid phase property
c	pertaining to coolant
i,j,k	indices
I	interfacial property
x	liquid phase property
y	vapour phase property
t	pertaining to total mixture

Superscripts

$\bullet$	transfer coefficient obtained under finite mass transfer rates
x	liquid phase property
y	vapour phase property
$\hat{\ }$	pseudo-property
$\bar{\ }$	partial molar quantity

References

1. G. Ackermann, Ver.Deutsch.Ing.Forschungsheft, 382, 1 (1937)
2. A.P. Colburn and T.B. Drew, Trans.Am.Inst.Chem.Engrs., 33, 197 (1937)
3. J.T. Schrodt, A.I.Ch.E.J., 19, 753 (1973)
4. K.J. Bell and M.A. Ghaly, A.I.Ch.E.Symp.Ser. No. 131, 69, 72 (1973)
5. H.L. Toor, A.I.Ch.E.J., 10, 460 (1964)
6. W.E. Stewart and R. Prober, Ind.Eng.Chem.Fundam., 3, 224 (1964)
7. R. Krishna and G.L. Standart, A.I.Ch.E.J., in press
8. E.N. Fuller, P.D. Schettler and J.C Giddings, Ind.Eng.Chem., 58, 19 (1966)
9. N.R. Amundson, *Mathematical Methods in Chemical Engineering*, Prentice Hall, Englewood Cliffs, N.J. (1966)