THE APPLICATION OF LIQUID THERMAL DIFFUSION AS A SEPARATION TECHNIQUE (1)

The separation of liquid mixtures by thermal diffusion has been regarded as uneconomical in comparison with other more conventional separation processes due to the high energy costs predicted by the available design equations. As a result, the applications of the technique have been essentially limited to laboratory operations as an analytical tool or in preparative-scale purifications. However, earlier analysis on the applications of the technique have not taken into account the very special characteristics of the thermal diffusion process, namely, the possibility of utilizing virtually any temperature gradient at any temperature level. Yet, this unique feature may be the key factor in determining the economic viability of industrial applications.

In the present work, the principal aspects concerned with the application of liquid thermal diffusion as a separation technique are examined for both batch and continuous operations and a new, semi-batch, type of operation is suggested. The available design methods are also discussed and a new approach for the design of continuous columns is proposed.

1 — INTRODUCTION

The application of liquid thermal diffusion as a separation technique has been mostly limited to small-scale operations where the output and heat requirements are not restrictive factors. In these cases, thermal diffusion columns have been used either as an analytical tool or in preparative-scale separations which cannot be accomplished by other more conventional methods [1-3]. In general, these operations are batchwise and the parameters to optimize are the degree of separation attainable and the time of operation.

In large-scale applications, however, besides the technical aspects it is necessary to estimate the economical viability of the process. Several pilot-plant studies and earlier industrial plants [4, 5] have demonstrated that large-scale continuous units do not pose any significant technical problem: they are easy to operate, almost trouble-free and the performance may be satisfactorily predicted by the phenomenological theory of the process or from small-scale experiments. Notwithstanding, industrial applications have failed to appear and the reasons must lie on the high energy costs predicted by current design methods which are based on the work of Krasny-Ergen [6] on the later 40's.

2 — THE FOUNDATIONS OF THE DESIGN

In small-scale operation the design of the equipment and the selection of the operating conditions are dictated solely by the technical aspects and therefore in most cases they are based on the phenomenological

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This paper was presented at the Transport processes section
equations of the batch column, in accordance with the particular objectives desired.

In the case of industrial (large scale) operations, however, it is necessary to optimize the column dimensions and the operating conditions in order to obtain the most economical solution. This is the aim of the earlier work of Krasny-ERGEN [6] and BENEDICT [7] and the more recent and simplified formulation of POWERS [8].

These authors considered two aspects of the problem:

1) The selection of the operating wall temperatures to minimize the heat transfer area and the heat input, and
2) The determination of the column dimensions that minimize the cost-function II defined by

\[ \Pi = \left[ S + \frac{P}{2\omega} \right] \int dA \]  

where \( S \) is the amount of fixed costs per unit of column area and \( \frac{P}{2\omega} \) is the power cost per unit of area and unit of time.

The first objective implies some recommendations which, in fact, tend to overload the power costs since the minimum amount of surface is secured by working with the greatest possible temperature difference between the hot and cold walls and the minimum heat input is secured by using an absolute hot wall temperature two to three times the absolute cold wall temperature. In practice, then, the hot wall must be of the order of 350 °C or more if tap water is used for cooling. But, this means that the process is virtually uncompetitive at those temperature levels due to its low thermodynamic efficiency [9] in comparison with other less energy-demanding separation techniques.

With regard to the determination of the most economical column dimensions for a given value of \( \Delta T \) — the second aspect of the design under consideration — it is of importance to analyse the cost-function II, namely in what respects the association of the power costs with the term \( \frac{P}{2\omega} \). The suggestion is that the power is consumed in producing the temperature gradient which is a slightly different way of putting the question.

Assuming further that the power costs are directly proportional to the gradient attained through the constant \( a \), it is possible to write

\[ \text{Power cost} = a \cdot \frac{\partial T}{\partial x} = a \cdot \frac{\Delta T}{2\omega} \]  

Noting that, in this aspect of the design, \( \Delta T \) is pre-fixed, the product \( a \cdot \Delta T \) is constant (represented by \( p \)). Hence

\[ \text{Power cost} = \frac{a \cdot \Delta T}{2\omega} = \frac{p}{2\omega} \]  

The conclusion expressed by equation (3) is not, however acceptable. In fact, the power costs are intrinsically associated with the heating and cooling of the column walls which is to say with \( \Delta T \). If, as in the present circumstances, the value of \( \Delta T \) is fixed, then the power costs become inescapably determined whatever the values of \( \omega \) or \( \frac{\partial T}{\partial x} \) may be. In other words, when the value of \( \Delta T \) is fixed, the changes in the value of \( \frac{\partial T}{\partial x} \) do not affect the power-costs but solely the performance of the column as predicted by the appropriate phenomenological equations.

The discrepancy between the implications of equation (3) and the reality is, indeed, a consequence of this other discrepancy: having first assumed — in establishing equation (2) — that the temperature gradient was the design variable, the subsequent developments and analysis are carried out in terms of other variables, in this case, \( \Delta T \) and \( \omega \).

It may then be concluded that the validity of the current design methods is, at least, doubtful and, an important «corollary» is that the comparisons that have been made in the literature between thermal diffusion and other separation techniques [7, 10] are impaired by the use of the above equations to predict thermal diffusion costs.

But, the existing assessments on the industrial viability of thermal diffusion as a separation technique become even more questionable when realizing that, probably the most important features of the technique have been systematically forgotten. Indeed, it is quite surprising that no mention has been made to the capability of the process to separate
mixtures at any temperature level and under any temperature gradient, the only factor affected being the time of operation or the ratio \((\sigma/B)\) but not the separation attainable. If, thus, instead of creating new powerful heat sources for use in thermal diffusion, cheap heat sources available are used without incurring in any significant extra-cost, then the process may work at virtually zero running costs and only the capital for the equipment is involved. Even the manpower required is practically negligible.

In referring to 'cheap heat sources available' it is meant 'non-used' heat sources like the solar energy for which simple devices of capturing the necessary heat may be arranged using existing methods [11] as shown in fig. 1. (Other «non-used» sources are, for instance, the geothermal energy where it occurs, or even the existing temperature gradient between the inside and outside of industrial and other buildings.) More frequently however, the available heat source is to be provided by other operations of heat transfer already existing in the industrial plant. In fact, the thermal diffusion column may be considered as an heat exchanger — see fig. 3 — and therefore it may be enclosed on the flow-circuits in parallel with existing heat exchangers, the net power consumption being in these circumstances much less than predicted by the design equations. An example where thermal diffusion could be used «on line» is the manufacture of ethanol by hydrogenation of ethylene whose flowsheet shown in fig. 2 indicates two possible locations of a thermal diffusion unit (in parallel with the cooler or the heater) to perform the purification of a fraction of the crude ethanol — see fig. 3.

Summarizing this section it may be said that:

1) Contrary to what has been currently accepted, the separation by thermal diffusion may be economically interesting.

![Fig. 1](image1.png)

**Fig. 1**

A means of using solar energy for heating a thermal diffusion column

![Fig. 2](image2.png)

**Ethanol synthesis flowsheet with the circles showing the possible locations of a thermal diffusion unit**

2) The approach for establishing a design procedure appears to be, now, substantially different from that of KRASNY-ERGEN [6] and BENEDICT [7]. In brief, the new premisses for design are:

a) The value of \(\Delta T\) is fixed by external conditions, namely, the heat source available.

b) The operation costs are essentially related to the equipment and maintenance costs.

![Fig. 3](image3.png)

**Fig. 3**

The analogy between a thermal diffusion column and an heat exchanger (ex. purification of crude ethanol)
3 — BATCH SEPARATION

3.1 — EQUATIONS

The batch separation of a binary mixture in a thermal diffusion column shows an evolution with the time of the type represented in fig. 4 where $\Delta_\infty$ is the equilibrium separation, assimptotically reached, and $t_r$ is the relaxation-time which, for the time being, may be defined as the time required to attain about 70 % of the steady-state separation.

![Fig. 4](image)

*Fig. 4*

The separation vs. time curve in batch operation

There are two regions of the separation curve of fig. 4 that may be expressed through simple equations derived from the phenomenological theory of the thermal diffusion column. The first is in the short time range such that

$$
t \leq \frac{(2\omega)^2 T_{av}^2}{14x^2(\Delta T)^2D} \cdot |\lambda|^{1.82}
$$

(4)

for which RUPPEL and COULL [12] obtained

$$
(\Delta)_{RC} = \frac{4c_o(1 - c_o) (\Delta T)\lambda}{45T_{av}(2\omega)} \sqrt{\frac{2835D}{2\pi}} \sqrt{vt}
$$

(5)

The other equation is for times

$$
t \geq 0.3t_r
$$

(6)

and was derived by HOFFMAN and EMERY [13]:

$$
\Delta = \Delta_\infty (1 - k_3 e^{-t/t_r})
$$

(7)

where $k_3$ is a coefficient that may generally be regarded as a constant and equal to $8/\pi^2$ with an error less than 1 %, and the exact values of $\Delta_\infty$ and $t_r$ are given by the following equations:

$$
\Delta_\infty = \frac{(e^{c_o\lambda} - 1) (e^{\lambda} - e^{c_o\lambda})}{e^{c_o\lambda} (e^{\lambda} - 1)}
$$

(8)

$$
t_r = \frac{10}{7} \frac{T_{av}^2(2\omega)^2}{x^2(\Delta T)^2D} \cdot \frac{1}{4} + \frac{\pi^2}{\lambda^2}
$$

(9)

and $\lambda$, the dimensionless length of the column is

$$
\lambda = \frac{504\pi D_\eta L}{\beta g T_{av}(2\omega)^4}
$$

(10)

In the case of small separations and moderately concentrated solutions for which the product $[c(1-c)]$ may be taken as constant, POWERS [14] obtained a more simple solution for the parameters $\Delta_\infty$ and $t_r$ in equation (7):

$$
\Delta_\infty = [c(1 - c)] \cdot \lambda \simeq 0.25\lambda
$$

(11)

$$
t_r = \frac{9!D_\eta^2 L^2}{\pi^2 \beta^2 g^2(\Delta T)^2(2\omega)^6}
$$

(12)

3.2 — APPLICATION OF THE «IDEAL» EQUATIONS TO «PRACTICAL» SEPARATIONS

The preceding equations are derived from the phenomenological theory of FURRY et al. [15] which involves several simplifying assumptions. The validity of these assumptions and of the theory has been fully discussed recently by HORNE and BEARMAN [16] and ROMERO [17, 18] and the conclusion is that they are essentially acceptable.
except in what concerns the constancy of the
distance between the walls. Indeed, ROMERO and
BOTT [19] confirmed earlier suggestions [13, 20]
that small eccentricities in the annular space do
affect the performance of a thermal diffusion
column and, as a result the phenomenological
equations derived for an «ideal» (perfect) column
were unable to describe the actual column. To
overcome the difficulty Bott and Romero introduced
the 'equivalent annulus width' concept — the annulus
width of a perfect column that gives the same
separation as the actual imperfect column, the other
variables being kept constant — based on the
analysis of the hydrodynamics of annular spaces
and on the influence of the flow pattern on separation
in thermogravitational columns.
In practice, the introduction of the 'equivalent
annulus width' means that the value of the wall
spacing to be used in the phenomenological equa-
tions, \(2w\), is not the same as the mechanically
measured distance \(r_2 - r_1\), but rather

\[
2\omega = (r_2 - r_1) \cdot \nu
\]

with \(\nu \geq 1\).
The determination of \(\nu\), which is constant for a
given column was presented in a recent paper by
ROMERO and PINHEIRO [21] where the experimental
evidence of the validity of the concept in correlating
experimental data is also shown.
As a result of the introduction of \(\nu\), the separation
equations maintain their functional dependences
on the variables predicted by the phenomenological
theory but, in fact, a new variable, \(\nu\) — the deviation
from geometric ideality —, must be considered
along with the distance \(r_2 - r_1\) when discussing
the effect of \(2\omega\) on separation.
Besides allowing for the correlation of experimental
data in terms of the phenomenological equations,
the equivalent annulus width concept is of great
utility in design since it enables the definition of
a degree of imperfection of the column which may
be evaluated by calibrating it with a «standard»
mixture and determining \(\nu\). On the other hand,
it is likely that low values of \(r_2 - r_1\) will yield
the larger values of \(\nu\), loosing therefore the eventual
benefits of a small wall distance [as shown by
equation (13)].

3.3 — THERMAL DIFFUSION

3.3.1 — THERMOGRAVITATIONAL COLUMNS

The two most popular and simple columns are
the parallel plate column and the concentric cylinder
column. The latter has the advantages of making
the heating and cooling of the walls more simple
and requiring less space. The parallel plate column
is more flexible from the point of view of changing
the wall distance. It also enables the column to be
operated with an inclination from the vertical or
with a packed annular space.
The purpose of inclining the column or using the
packing is to deflect the particles streamlines thus
reducing the convective flow and the remixing
associated with it. The separation attainable at the
equilibrium is enhanced in both the inclined and
packed columns as compared to the conventional
apparatus, but the time of operation required is
also greatly increased, and therefore the gain is
not much.
The equations describing the inclined column may
be obtained from the conventional column equations
by substituting the gravity field component \(g\) by
\(g \cos \theta\) where \(\theta\) is the deflection angle from
vertical. The optimum angle of inclination is
evaluated by setting \(\frac{\partial \Delta}{\partial \theta} = 0\) and solving for \(\theta\).
This column was studied by POWERS [22] and
CHUEH and YEH [23] who were able to confirm
the theory experimentally.
A phenomenological theory for the packed column
has been proposed by LORENZ and EMERY [24]
but the experimental data has not always agreed
with the theory [24, 25]. This, however may be
due, in part, to the difficulties in handling the
packing in the very narrow gap which results in
poor reproducibility in the experimental conditions.
Other types of columns make use of barriers [26]
or a wire wrapped along the inner cylinder of a
concentric apparatus [27] but, besides its intrinsic
complexity of construction they do not show any
real improvement relatively to the other types
mentioned.

3.3.2 — NON-THERMOGRAVITATIONAL COLUMNS

Since the transport process in a thermal diffusion
column results from the combination of the demixing
in the horizontal direction with the vertical convec-
tion it is conceivable that other driving-forces than the thermal gradient have been used to promote the transport in either the horizontal or vertical direction. VON HALLE [28], for instance, used a column where the convection is obtained with an external reflux; BEAMS [29] and RAMSER [30] suggested the use of moving walls (in opposite direction) to obtain a Couette flow in the annular gap. More recently POWERS et al. [31] used an electrical field in the horizontal direction together with the thermal convection. In some cases, these apparatus may produce better separations than the thermogravitational ones but in most cases this is not so. Noting, furthermore, that these columns are not easy to operate its use in practice is not usually recommended.

3.3.3 — ROTARY COLUMN

This type of apparatus, first used by SULLIVAN et al. [32] only recently has received the attention of the investigators in the field [32-36]. Its hydrodynamics are rather more complex than those of the conventional static column due to the 3-dimensional flow pattern inside the annular space. The experimental reports so far published appeared to be in poor agreement, but, quite recently, a phenomenological theory has been presented that not only explains the experimental data published but also indicates the variables that govern the performance of such a column, for speeds of rotation $\geq 10$ RPM.

Using the same basic arguments presented by BOTT and ROMERO [19] to introduce the equivalent annulus width concept, BOTT and PINHEIRO [37] defined a correction factor, $\Phi$, that is a function of the factor $v$ previously referred and the speed of rotation, $N$.

The actual parameters to use in the Hoffman and Emery-type equation are (the asterisk means rotary)

$$\lambda^* = \frac{1.43}{\Phi} \lambda$$

(14)

$$t_r^* = t_r \cdot \frac{21}{25} \Phi \frac{0.25 + \pi^2/\lambda^2}{0.25 + \pi^2/\lambda^2(\Phi/1.43)^2}$$

(15)

For the short time range an equation similar to the Ruppel and Coull’s is also written as

$$\Delta_{RC}^* = \Delta_{RC} \left( \frac{1.2}{\Phi} \right)^{1/2}$$

(16)

In all equations,

$$\Phi = \Phi(v, N)$$

(17)

and

$$\Phi \geq 1$$

(18)

In fig. 5, the effect of parameters $v$ and $N$ upon $\Phi$ is shown.

The above equations correlated earlier experimental data of ROMERO [33] and PINHEIRO [36] very satisfactorily and the parameter $\Phi$ — which in fact determines the actual improvement (or not) relatively to the static column — proved to be quite adequate to describe the column behaviour. Briefly, it may be said that if the column is not too imperfect the separation is improved by rotation, the maximum being dependent on the mixture properties and on the value of $\Phi$ [37].

3.4 — BATCH OPERATION DESIGN

The characteristics of the apparatus and the selection of the experimental conditions are, naturally,
dependent on the purpose of the operation. As mentioned before, the batch separation is generally associated with small-scale operations where the thermal diffusion technique is used as an analytical tool or as a preparative-scale process. In both cases, however, the emphasis is on the separation attainable and the time it requires. Other characteristics like the ease of operation and control and the flexibility to work with different types of systems at different temperatures, are also desirable.

As a first approximation, equations (10) and (11) may be used to conclude that the maximization of $\Delta$ implies the increase of the ratio $[L/(2\omega)^4]$, that is, of $\lambda$. But, since that ratio involves the 4th power of $(2\omega)$ the best way of increasing it is by decreasing the value of $(2\omega)$ which, according to equation (13) implies the decrease of the distance between the walls $(r_2 - r_1)$, and/or a decrease in the «imperfection factor» $\nu$. This factor is likely to increase with the increase of the ratio $(L/2\omega)$ and if its value is to be kept close to unity one must expect an heavier burden on the construction costs.

As a guideline from the experience and from the analysis of published data it may be recommended that the value of $(r_2 - r_1)$ should not be lower than about 0.04 cm if the column height does not exceed about 2 m. In practice this will yeld, on average, a value for the equivalent annulus width, $2\omega$, of the order of 0.05 — 0.07 cm. For smaller values of $L$ the value of $2\omega$ will tend to be 0.04 cm.

This «lower limit» of $(2\omega)$ is also advisilable in terms of the time required for the separation. In fact (noting that for these range of values of the annulus width equations (9) and (12) are identical) equation (12) shows how strongly the value of the relaxation time is affected by $(2\omega)$.

In what concerns the heating and cooling of the column walls it is recommended that, whenever the range of temperatures allows it, circulating fluids should be used preferably to electrical wires wrapped along the walls, since the former offers a much better homogeneity [38] and thermal irregularities are likely to increase the value of $\nu$ [20].

It is also recommended that the design should allow for several sampling parts along the column length not only to obtain different fractions in multicomponent mixtures but also to allow for the semi-batch operation to be carried out.

3.5 — SEMI-BATCH OPERATION

In many cases the separation vs. time curve has a high inclination in the short experimental times and then flattens out in a very short period as shown in fig. 6. In these situations only the time $t_1$ is required to reach a degree of separation close to $\Delta_\infty$.

![Fig. 6](image)

The separation vs. time curve for small values of the relaxation-time

In general, the times $t_1$ are within the range where the Ruppel and Coull equation applies and it is seen, from equation (5) that in this period the column length is not an important variable, i.e. it is possible to use a relatively short column with a smaller value of $(2\omega)$. The operating variables in this case are the temperature difference, $\Delta T$, and the annulus width, $2\omega$, or more precisely the ratio $(\Delta T/2\omega)$. It is seen that now, the value of $(2\omega)$ is not so decisive as in the batch operation — equations (10) and (11) — where it is elevated to the 4th power, and also that the value of $(\Delta T)$ may be manipulated in order to increase the separation in the time $t_1$.

It is thus possible to withdraw, at the time $t_1$, the top and bottom fractions each of which has on average a difference of about $(\Delta 1/2)$ from the initial concentration. The volume withdrawn is then replaced with fresh mixture and new top and bottom fractions withdrawn and now after a time $t_2 < t_1$ (since the process was already initiated) and with the composition of the fractions equal to those for $t = t_1$.

It is possible in this manner to obtain relatively
large amounts of purified products with a composition of \((c_o \pm \Delta 1/2)\) in a relatively short period of time. The operation may be taken further if the column is loaded with purified fractions. This is shown in fig. 7 where \(\Delta t\) and \(\Delta b\) are the separations obtained in the «top-fractions» and «bottom-fractions» columns, respectively. At the end, then the purified top and bottom products have compositions of, respectively

\[
c_t = c_o + \frac{(\Delta t + \Delta t)}{2}
\]

and

\[
c_b = c_o - \frac{(\Delta t + \Delta b)}{2}
\]

If a series of 3 columns is used it is also possible to conceive a «reflux» which carries material whose composition differs from the fresh feed, \(c_o\), and therefore enter the column at different points.

The semi-batch operation is, in fact, a bridge between the small-scale batch operation and the large-scale continuous process. Its use in the laboratory preparative-scale is however fully justified by the difficulties encountered in running the small-scale equipment continuously, due mainly to the extremely low product flow-rates that are imposed by the separation required (usually high) and the apparatus dimensions.

4 — CONTINUOUS SEPARATION

4.1 — EQUATIONS

The discussions on this operation shall be restricted to the case where the product \([c \{1 - c\}]\) may be taken as constant, i.e. where the initial feed concentration is not far from equimolarity and the degree of separation less than about 50 \(\%\).

It is also considered, according to the work of Powers and Wilke [39] that the process occurring in the upper section of the column (enriching section, subscript «e») are symmetrical to those of the lower section (stripping section, subscript «s») regardless of the location of the feed. This means that it is possible to discuss only one half of the column with a length \(L/2\) and a product flow rate \(\sigma_{av}\) such that

\[
\sigma_{av} = \frac{(\sigma_e + \sigma_s)/2}{\sigma_e \cdot \sigma_s}
\]

The separation equation for the continuous thermal diffusion column was first derived by Furry et al. [15, 40] as an extension of the batch theory. Later, Powers and Wilke [22] and Emery [41] suggested some modifications to take into account the variation of the vertical concentration gradient with the horizontal distance. However, for the usual range of product flow-rates involved both the Powers and Wilke and Emery approaches reduces to the classical equation of Furry et al. [40].

\[
\Delta = \frac{2c(1-c)H}{\sigma_{av}} \left[ 1 - \exp \left( - \frac{\sigma_{av} \cdot L}{2K} \right) \right]
\]

where \(H\) and \(K\) are transport coefficients given by

\[
H = \frac{\alpha^2 \rho g B(\Delta T)^2(2\omega)^3}{6!T_{av}\eta}
\]

\[
K = \frac{\beta^2 \rho g^2 B(\Delta T)^2(2\omega)^7}{9!D\eta^2}
\]
LIQUID THERMAL DIFFUSION

As discussed earlier, the eccentricity of the annular space decreases the separation and increases the relaxation time of the batch separation. Considering that the batch operation is the limiting case of the continuous process when \( \sigma = 0 \), it appears that the «equivalent annulus width» concept must also be introduced in the case of continuous columns. Yet, it is also apparent that as the natural convection becomes less important, i.e. when the product flow rate increases, the influence of the factor \( \nu \) (associated with the natural convection) becomes less significant and, in the limit when the flow in the enriching section is solely upwards (and in the stripping section, downwards) the influence of \( \nu \) is null (for this case also \( \Delta = 0 \)).

From the velocity profile in a continuous column

\[
v_z = \frac{\beta g(\Delta T)\omega^2}{12\eta} \left[ \xi - \xi^3 + r(1 - \xi^2) \right]
\]

where \( \xi \) the dimensionless horizontal distance is

\[
\xi = x/\omega
\]

and \( r \), the «relative product rate» is

\[
r = \frac{9\sigma v \eta}{\beta \rho g B(\Delta T)\omega^3}
\]

it is seen that the limits of the continuous operation are defined by \( r \) which, in fact, is a measure of the relative importance of the forced flow:

\[
r = 0 \Rightarrow v_z = (v)_\text{batch}, \quad \Delta = (\Delta)_\text{batch}, \quad \nu = (\nu)_\text{batch}
\]

\[
r = 1 \Rightarrow (v)_e \leq 0, \quad (v)_h \geq 0, \quad \Delta = 0, \quad \nu = 0
\]

Assuming that the value of \( \nu \) varies linearly with \( r \) it is then possible to write, for a continuous column

\[
\nu = (\nu)_\text{batch}(1 - r) + r
\]

Considering then, that \( 2\omega = (r_2 - r_1) \) and using \( \nu \) explicitly, the separation equation becomes

\[
\Delta = \frac{2c(1 - c)H}{\sigma_{av}} \nu^3 \left[ 1 - \exp \left( -\frac{\sigma_{av}L}{2K} \cdot \frac{1}{\nu^7} \right) \right]
\]

and it may be shown that it represents the experimental data of Powers and Wilke [22] better than the classical solution (without using \( \nu \)). In practice, the operation will in general be conducted in the small flow-rates region where the value of \( \Delta \) remains sufficiently high to be interesting. In this case, the exponential in equation (31) may be expanded in a series whose terms beyond the third may be neglected.

Thus, for

\[
\frac{\sigma_{av}L}{2K\nu^7} < 0.5
\]

equation (31) may be simply written, with an error less than 2 %, as

\[
\Delta = c(1 - c) \cdot \frac{HL}{K} \cdot \frac{1}{\nu^4} \left( 1 - \frac{\sigma_{av}L}{4K\nu^7} \right)
\]

or, in terms of the steady-state batch separation, \( \Delta_\infty \)

\[
\Delta = \Delta_\infty \left( 1 - \frac{\sigma_{av}L}{4K\nu^7} \right)
\]

4.2 — DESIGN EQUATIONS

It is of convenience to write equation (33) in a slightly different form to emphasise the dependences on the operating (design) variables:

\[
\Delta = a_1 \frac{L_m}{(2\omega)^4} \left[ 1 - \frac{\sigma_m L_m}{a_2 B_m (2\omega)^7} \right]
\]

\[
a_1 = \frac{504\pi D\eta}{4\beta g T_{av}} \cdot 10^2
\]
\[
a_2 = \frac{4g^2 \rho g^2}{9!Dv^2} (\Delta T)^2 \cdot 60
\]  
\[ \tag{37} \]

\[
2\omega = r_2 - r_1
\]  
\[ \tag{38} \]

and \(L_m\) and \(B_m\) are the column length and the column width in meters and \(\sigma_m\) is the mean product flow rate in g/min.

It is thus seen that both \(T_{av}\) and \((\Delta T)\) are not considered design variables since, according to section 2, these are fixed by the cheap heat sources available.

It is now possible to obtain the value of \(2\omega\) that maximizes the separation in terms of the other design variables by setting \(\partial\Delta/\partial(2\omega v) = 0\). This yields

\[
(2\omega v)_{opt} = \left(\frac{11}{4a_2}\right)^{1/7} \cdot \left(\frac{\sigma_m L_m}{B_m}\right)^{1/7}
\]  
\[ \tag{39} \]

Using this value in equation (35) and making

\[
a_3 = \frac{7a_1}{11} \left(\frac{4a_2}{11}\right)^{4/7}
\]  
\[ \tag{40} \]

the following equation is obtained

\[
\Delta_{max} = a_3 L_m^{3/7} \left(\frac{B_m}{\sigma_m}\right)^{4/7}
\]  
\[ \tag{41} \]

which gives the relations between the variables that yield the maximum separation.

If the degree of separation required, \(\Delta^*\), is prefixed then it is possible to write

\[
\frac{\sigma_m}{B_m} = \left(\frac{a_3}{\Delta^*}\right)^{7/4} L_m^{3/4}
\]  
\[ \tag{42} \]

and, substituting this value into equation (39) it is obtained, after rearranging

\[
\frac{L_m}{(2\omega v)_{opt}} = \frac{\Delta^*}{7a_1/11}
\]  
\[ \tag{43} \]

which emphasises the interdependence between the values of \(L_m\) and \((2\omega v)\) for optimum conditions. Similarly, equation (42) shows how the values of \(\sigma_m\) and \(B_m\) are strongly related.

Equations (42) and (43) are, in fact, those that govern the basic dimension of the equipment, together with the limits to \((2\omega)\), \(L_m\) and \(B_m\) dictated by the construction costs and by the values of the parameters \(a_1\) and \(a_2\).

When the degree of separation and the product flow rate are both pre-fixed at values of \(\Delta^*\) and \(\sigma^*\) it is possible to write equation (42) as

\[
(\sigma^*)^{4/7} \cdot \Delta^* = a_3 L_m^{3/7} B_m^{4/7}
\]  
\[ \tag{44} \]

or, noting that \(L_m\) and \(B_m\) are of the same order of magnitude and that the product \((L_m B_m)\) is half the area of the column, \(A\),

\[
(\sigma^*)^{4/7} \cdot \Delta^* \simeq \frac{a_3}{\sqrt{2}} \sqrt{A}
\]  
\[ \tag{45} \]

which gives an indication of the area required to perform a given separation with a given output when the value of the annular space is at the optimum.

It is also worth noting that parallel plate columns are in general, preferable to concentric cylinder apparatus due to the higher values of \(B_m\) they allow. This remark is in contradiction with earlier recommendations of using bundles of concentric columns in an heat-exchanger-type arrangement [5, 8].

In many cases it is not possible to achieve the desired degree of separation with one column and it is necessary to use a series of columns through which the mixture is passed. There are several types of arrangements, depending on the output and separation required but those that appear to be the most successful are the «cascade» [40] and the «transverse flow pattern» [42] arrangements.

These types of column batteries require themselves an optimization treatment to obtain the best overall performance but in what concerns the optimization of each individual column the above treatment remains essentially valid.

Before finalizing it must be said that with this new approach, based on the argument that thermal
diffusion may be used in large-scale without incurring in any new extra power-cost, the operation costs are solely related with equipment costs — materials + construction + maintenance and depreciation — which are likely to be given by equations of the type

\[ \text{Materials cost} = C_1(2L_mB_m) = C_1A \]  
\[ \text{Labour cost} = C_2 \cdot \frac{L_m}{2\omega} \cdot \frac{B_m}{2\omega} = \frac{C_2}{(2\omega)^2} \cdot A \]  
\[ \text{Fixed cost} = S \]

and therefore, the operation cost is

\[ \Pi = \left[ C_1 + \frac{C_2}{(2\omega)^2} \right] \cdot A + S \]  

which, indeed is quite different from that predicted by equation (1).

**LIST OF SYMBOLS**

**A** — column area  
**a** — constant eq. (2)  
**a_1** — coefficient defined by eq. (36)  
**a_2** — coefficient defined by eq. (37)  
**a_3** — coefficient defined by eq. (40)  
**B** — column width  
**C_1** — coefficient eq. (46)  
**C_2** — coefficient eq. (47)  
**c** — molar fraction of the reference component  
**c_0** — feed composition  
**D** — ordinary diffusion coefficient  
**g** — gravity acceleration  
**H** — transport coefficient defined by eq. (23)  
**K** — transport coefficient defined by eq. (24)  
**k_3** — coefficient eq. (7)

**GREEK LETTERS**

\( \alpha \) — thermal diffusion factor  
\( \beta \) — \( \partial \phi / \partial T \)  
\( \Delta \) — degree of separation between the top and bottom of the column  
\( \Delta x \) — steady-state separation  
\( \Delta T \) — temperature difference between the walls \( (T = T_2 - T_1) \)  
\( \eta \) — viscosity  
\( \theta \) — deflection angle from the vertical  
\( \lambda \) — dimensionless length defined by eq. (10)  
\( \nu \) — «equivalent annulus width» factor, eq. (13)  
\( \xi \) — dimensionless horizontal distance, eq. (26)  
\( \Pi \) — cost-function  
\( \pi \) — 3.141592...  
\( \rho \) — density of the mixture  
\( \sigma \) — product flow-rate  
\( \Phi \) — rotary column factor, eqs. (14) to (18)  
\( \omega \) — half distance between the column walls

**SUBSCRIPTS**

**av** — average values  
**b** — bottom fraction of the column  
**t** — top fraction of the column  
**m** — in meters  
**e** — enriching section  
**s** — stripping section  
**RC** — Ruppel and Coull  
**max** — maximum  
**opt** — optimum

**SUPERSCRIPTS**

\( * \) — rotary column parameter  
\( \# \) — pre-fixed value
REFERENCES


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RESUMO

A separação de misturas líquidas por difusão térmica tem sido considerada com reduzido interesse económico em comparação com outros processos de separação mais conhecidos. As aplicações da técnica não são limitadas ao domínio da química, nem ao laboratório, mas podem ser aplicadas em várias áreas, incluindo a separação de misturas de fluidos complexos, como misturas de petróleo e gás natural. A técnica é particularmente interessante para a separação de misturas de líquidos em operação contínua, descontínua e semicontínua.

As características únicas do processo de difusão térmica, nomeadamente a sua capacidade de separar componentes de uma mistura a qualquer nível de temperaturas, tornam-na uma técnica muito promissora. No entanto, é importante salientar que a aplicação prática da difusão térmica enfrenta vários desafios, incluindo a necessidade de um projeto de instalações adequado e a optimização dos parâmetros operacionais.