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A theoretical study of laser-heated thermal diffusion columns

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Abstract. The operation of a laser-heated thermogravitational column is theoretically analysed. Attention is focused on columns to be used to measure thermal diffusion factors in liquid mixtures. It is found that the steady separation is quite insensitive to the ratio of the light beam semi-width to the tube radius. The comparison with the results for concentric-tube type columns shows that it is possible to design small laser-heated columns having separations and relaxation times similar to the conventional units currently used to determine thermal diffusion factors.

1. Introduction

During the last few years some authors (Klein *et al* 1981, Arisawa *et al* 1982) have reported both theoretical and experimental work on the separation of gas mixtures in laser-heated (LH) thermogravitational columns. Laser light absorption in the gas, instead of the conventional Joule heating of an axially installed wire, furnishes the primary non-uniform temperature field that is needed for the subsequent segregation of the mixture. The above work emphasises aspects related to the separation of both isotopic and non-isotopic mixtures.

The present paper is concerned with a theoretical analysis of the potential advantages of the mode of light heating in the operation of thermal diffusion (TD) columns specifically designed to measure Fickian and thermal diffusion coefficients, D and D_T, of liquid mixtures. At present, it is well established that the theory giving the relevant peculiarities of the separation process in concentric-tube (CT) columns is accurately supported by experimental results (Horne and Bearman 1968, Stanford and Beyerlein 1973, Navarro *et al* 1985, Ecenarro *et al* 1989). Corrections for non-ideal geometry and density effects (*forgotten effect*) can also be properly accounted for, as has recently been proved (Ecenarro *et al* 1990). Although the light heating induces temperature fields quite different from those established through the Joule effect, the remaining physical mechanisms that lead to the final separation are identical in both cases. All this makes the problem particularly amenable for a theoretical description along the same lines as the standard theory for CT columns first given by Furry *et al* (1946). Figure 1 shows a line drawing of the idealised CT and LH columns.

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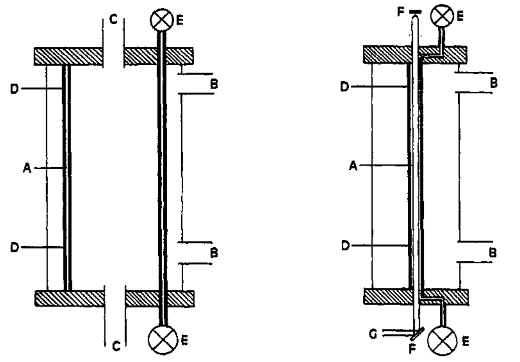

Figure 1. A line drawing of the CT and LH liquid thermal diffusion columns. A, working space; B, connections to circulating cooling water; C, connections to circulating heating water; D, sampling ports; E, filling and draining connections; F, mirrors; G, heating laser beam.

In standard TD practice, the separation units are designed to give a high amplification of the elementary separation effect, which is usually very small. This task is conveniently accomplished by using units of *quasi-plane* geometry, i.e. with a value of the ratio of the radii of the two concentric tubes very close to unity and consequently very small annular gap width. In these units the steady-state Rayleigh separation factor between the column ends, q, depends on the total column length, L, and on the width of the annular gap, w, as $\ln q \propto Lw^{-4}$. For this reason, large columns with small gap width are currently selected. Typical values of column dimensions are: $L = 250$ mm and $w = 1$ mm. However, this selection has two serious drawbacks. The first one is the well known constructional difficulty that such a design presents. The other is the undesirably long separation time associated with the *quasi-plane* geometry. It must be remembered that the characteristic time, t_r, is of the order of $t_r \propto L^2w^{-6}$, which does not favour a reasonable compromise between high separation and short time.

In the present theoretical treatment of light-heated TD columns some restrictive assumptions are used. It is assumed that: (i) the temperature differences in the fluid mixture are sufficiently small that the temperature dependence of the physical properties can be ignored; (ii) the vertical attenuation of the heating light beam is low enough that all the column cross sections can be considered to be in a thermally equivalent situation; and (iii) axial remixing effects due to vertical Fickian diffusion in liquid mixtures can be safety neglected. Assumptions (i) and (iii) are the standard ones in the theoretical treatment of liquid columns (Horne and Bearman 1968). The second assumption only holds for small optical densities (Scholz 1987).

These basic assumptions are applicable under the usual working conditions to determine D and D_T from column separation measurements and allow one to compare the results obtained with the previous ones reported by Slieker (1965) for CT columns. In particular, it is found that LH units of small size have performances of the same order as the standard CT columns.

2. Light heating

Under the assumptions quoted above, the temperature field is given by the solution of the stationary heat equation

$$\kappa \nabla^2 T = \varphi(r, z) \tag{1}$$

where T is the temperature, κ is the thermal conductivity of the mixture, φ is the strength of the local heat sources, and r and z are cylindrical coordinates in the tube. For a light beam weakly attenuated in its path along the column, $\partial_z \varphi = 0$. Moreover, it seems reasonable to accept a heat source distribution of Gaussian type,

$$\varphi(r) = (Q/2\pi\sigma^2)\exp(-r^2/2\sigma^2) \tag{2}$$

where σ is the semi-width of the light beam, and Q is the total heat amount being deposited into a fluid slab of unit length and very large radius. Actually, only a fraction of this power, Q_R/Q, is absorbed in each cross section of the tube of radius r_1. By integrating equation (2) we get

$$Q_R/Q = 1 - \exp(-r_1^2/2\sigma^2). \tag{3}$$

The solution of equations (1) and (2) gives the temperature field inside the separation tube. The required boundary conditions are: (i) $T = T_1$ at $r = r_1$, and (ii) the temperature must remain finite on the axis of the tube. In terms of the non-dimensional quantities

$$x = r^2/2\sigma^2 \qquad x_0 = r_1^2/2\sigma^2 \tag{4}$$

we obtain for the temperature distribution

$$T - T_1 = \Delta T[1 - f(x)/f(x_0)] \tag{5}$$

where

$$f(x) = \int_0^x [\exp(-x) - 1]\,\mathrm{d}x/x = -[E(x) + \ln x + \gamma] \tag{6}$$

and

$$\Delta T = T_2 - T_1 = Q/4\pi\kappa f(x_0). \tag{7}$$

Here T_2 is the temperature at the centre of the tube, $E(x)$ is the exponential integral and γ is the Euler constant. The temperature difference ΔT will be taken in the following as an indirect estimate of the heating effects of a given light beam into the particular chosen geometry. The values of $E(x)$ required in the numerical calculations were obtained from the literature. According to equations (5) and (6) for small values of x_0, the temperature profiles are linear in x. This limit case will be considered later. Large deviations from linearity arise for $x_0 > 1$.

3. The convection field

The convection pattern is obtained by solving the Navier–Stokes equation in the Boussinesq approximation. For a velocity field in the form $v_z \equiv v = v(r)$, we have the hydrodynamic equation

$$\eta^*\nabla^2 v = \rho g + \partial_z p \tag{8}$$

where ρ is the density, η^* the viscosity, p the fluid pressure and g the acceleration of gravity (starred fluid properties are to be evaluated at the mean temperature). By assuming, as customary, the density to be a linear function of T, and taking into account that the Poiseuille-like term does not depend on r, equation (8) in terms of x is

$$\mathrm{d}_x[x\,\mathrm{d}_x v] = \lambda[f(x) + \text{constant}] \tag{9}$$

where

$$\lambda = \rho^*\beta^* g\sigma^2 \Delta T/2\eta^* f(x_0)$$

β^* being the thermal expansivity coefficient. The velocity v must remain finite at $x = 0$ and cancels out at $x = x_0$. Under the two boundary conditions, the solution of equation (9) is

$$v(x) = \lambda[F(x) - F(x_0)] \tag{10}$$

where the function $F(x)$ is given by

$$F(x) = f(x) + xf(x) + [\exp(-x) - 1] + Cx. \tag{11}$$

The constant C is to be obtained by demanding mass flux cancellation through each cross section of the tube. In terms of the flow function defined by

$$g(x) = \lambda^{-1} \int_0^x v \, dx \tag{12}$$

this condition is equivalent to $g(x_0) = 0$.

Introducing equation (10) into equation (12) and integrating, we obtain for $g(x)$

$$g(x) = [x^2 f(x) + 2xf(x) + (x+1)\exp(-x) + x^2/2 + Cx^2 - 2F(x_0)x - 1]/2. \tag{13}$$

The flow pattern calculated from the above expressions correspond to an upwards hot flow close to the symmetry axis of the tube, which is balanced by a return cold fluid current descending close to the tube wall.

4. The column transport coefficients

Knowledge of the temperature field and the convection pattern allow determination of the thermodiffusive and convective column coefficients H and K_c, respectively, which are the quantities relevant in evaluating the column separation. These coefficients appear in calculating the transport of species through a column cross section from the continuity equation (Ecenarro *et al* 1989). In the Slieker (1965) notation, they are given for cylindrical geometry by

$$H = -2\pi \int_0^{r_1} \left[\alpha\, \partial_r(\ln T) \left(\int_0^r \rho\, v r \, dr\right)\right] dr \tag{14}$$

$$K_c = 2\pi \int_0^{r_1} \left[(\rho D)^{-1} \left(\int_0^r \rho v r \, dr\right)^2\right] dr/r. \tag{15}$$

Introducing equations (4), (5) and (12) into equations (14) and (15), the coefficients H and K_c can be written as customary in the form

$$\begin{aligned} H &= (2\pi/6!)(\alpha^* \rho^{*2} \beta^* g/\eta^*)[(\Delta T)^2/T^*]\, r_1^4 h \\ K_c &= (2\pi/9!)(\rho^{*3} \beta^{*2} g^2/\eta^{*2} D^*)(\Delta T)^2 r_1^8 k \end{aligned} \tag{16}$$

where h and k are the so-called column *shape factors*, which only depend on x_0 and are given by

$$h = (6!/8)[1/(x_0^2 f^2(x_0))] \int_0^{x_0} f_x(x) g(x) \, dx \tag{17}$$

$$k = (9!/128)[1/(x_0^4 f^2(x_0))] \int_0^{x_0} [g(x)]^2 \, dx/x. \tag{18}$$

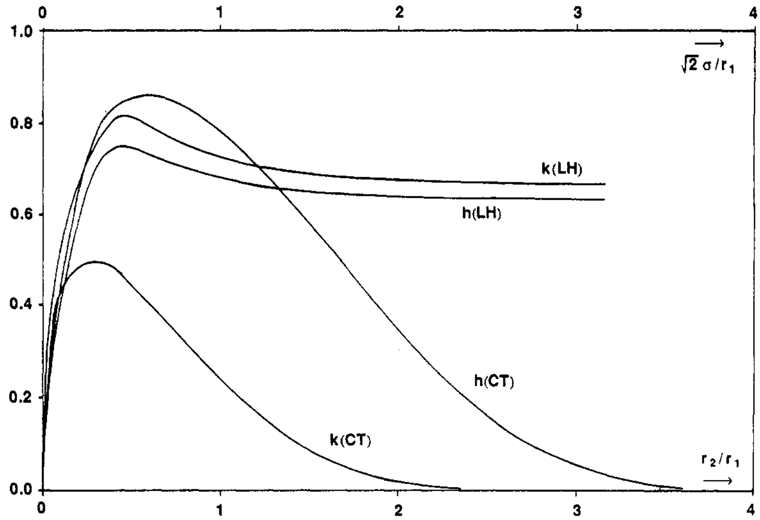

Figure 2. Shape factors h and k for the LH and CT cases. The quantities $4h$, $4k$ and $4(r_2/r_1)$ are actually displayed for the CT case.

Although the calculation of h and k can be performed analytically, it does not offer any particular advantage and we have done it numerically. The results are displayed in figure 2, for purposes of comparison with the corresponding results for CT columns, as a function of $\sqrt{2}\,\sigma/r_1$. As can be seen, both coefficients vanish for $\sqrt{2}\,\sigma/r_1 \to 0$ and tend to constant values for $\sqrt{2}\,\sigma/r_1 \geqslant 1$.

5. Results for concentric-tube columns

Results for the CT case have been previously reported by Slieker (1965). However, it is pertinent to quote some of them here in order to make the comparison between the two heating modes easier.

The temperature field is now given by

$$T - T_1 = \Delta T \ln y/\ln y_0 \tag{19}$$

with

$$y = (r/r_1)^2 \qquad y_0 = (r_2/r_1)^2 \tag{20}$$

where r_1 and r_2 are the radii of the outer and inner tubes, respectively. The solution of equation (8) gives the corresponding velocity field. One obtains

$$v = \lambda\,[y \ln y + A(1-y) + B \ln y] \tag{21}$$

where λ is here

$$\lambda = -(r_1^2 \rho^* \beta^* g \Delta T)/(4\eta^* \ln y_0)$$

and

$$\begin{aligned} A &= \ln y_0\,[1 - y_0^2 - 4y_0(1-y_0) - 2y_0^2 \ln y_0]/[D(1-y_0)] \\ B &= [(y_0^2 - 1) - 2y_0 \ln y_0]/D \\ D &= 2\ln y_0\,(1+y_0) + 4(1-y_0). \end{aligned} \tag{22}$$

Introducing the temperature and velocity fields in equation (14), in terms of the flow function defined by

$$g(y) = \lambda^{-1} \int_{y_0}^{y} v \, \mathrm{d}y \tag{23}$$

we obtain for the shape factors corresponding to CT columns the following expressions:

$$\begin{aligned} h &= (6!/8)[1/(\ln y_0)^2] \int_{y_0}^{1} g(y) \, \mathrm{d}y/y \\ k &= (9!/128)[1/(\ln y_0)^2] \int_{y_0}^{1} [g(y)]^2 \, \mathrm{d}y/y. \end{aligned} \tag{24}$$

Figure 2 shows the numerical results obtained for h and k as a function of r_2/r_1.

The Slieker (1965) paper also includes the diffusion remixing coefficient K_d, which does not contain any hydrodynamical flow feature and is relevant in the case of gaseous mixtures. Evaluating the fluid properties at the mean temperature, the coefficient K_d in a CT unit is given by

$$K_\mathrm{d} = \pi\rho^* D^* r_1^2(1 - y_0^2) \tag{25}$$

where y_0 must be replaced by zero for LH columns.

When TD units are used in separation tasks, large ΔT values are required. Thus, it is doubtful that the present formulation can be used to describe such situations correctly. On the contrary, the measurement of D and D_T coefficients is performed in columns with relatively small ΔT values. This fact, added to some previous work by our group (Navarro *et al* 1983), allows one to use the foregoing theoretical results confidently.

6. The column separation

The overall separation between the column ends is currently measured by the Rayleigh separation factor, q. At steady state, it is given by

$$\ln q = HL/K_\mathrm{c} = (9!/6!)(\alpha^* D^* \eta^*/\rho^* \beta^* T^* g)(L/r_1^4)(h/k) \tag{26}$$

where L is the column total length. Equation (26) shows that the shape factor combination relevant in the steady-state separation is just h/k. Figure 3 displays the values of h/k for LH and CT heating modes. For the LH case, this quantity is about unity and changes little in all the range of $\sqrt{2}\,\sigma/r_1$. On the contrary, for CT columns, h/k increases strongly with r_2/r_1. In particular, for $r_2/r_1 \simeq 1$, h/k tends to infinity as $[1 - (r_2/r_1)]^{-4}$ (see below), and then equation (26) gives for the steady-state separation the well known dependence with the annular gap width, w,

$$\ln q \propto L w^{-4}.$$

On the other hand, it has been reported (Ecenarro *et al* 1990) that the time evolution of the separation, with the exception of the earlier stages of the process, is well described by an exponential growth with a characteristic relaxation time constant, t_r, given by

$$t_\mathrm{r} = \mu L^2/\pi^2 K_\mathrm{c} \tag{27}$$

where μ is the fluid mass per unit length. Taking into account equation (16) for K_c, we obtain for CT columns

$$t_\mathrm{r} = (9!\eta^{*2} D^*/\pi^2 \rho^{*2} \beta^{*2} g^2)(L/\Delta T)^2 (r_1^2 - r_2^2)/(r_1^8 k) \tag{28}$$

and the same expression holds for the LH case by using the corresponding shape factor

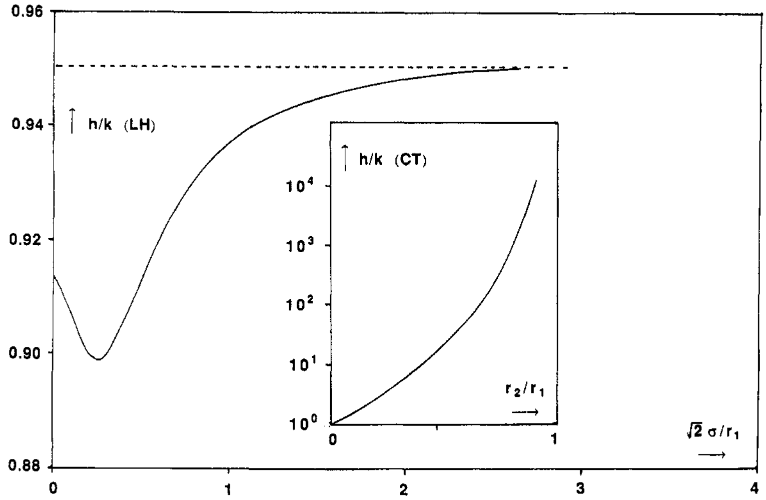

Figure 3. Values of h/k for LH and CT modes.

k and taking $r_2 = 0$. When non-active spaces or forgotten effect are to be accounted for, actual values of t_r are obtained from equation (28) through suitable correction factors available in the literature (Ecenarro *et al* 1990).

7. Limit cases

For CT units, there are two geometrical limit cases that correspond to $r_2/r_1 \simeq 1$ and $r_2/r_1 \simeq 0$. These were so-called by Furry *et al* (1946) the *plane case* and the *extreme cylindrical case*, respectively. It is useful to obtain approximate expressions of h and k for these two cases. For the plane case, the comparison of the well known results of Furry *et al* with equations (16) yields

$$h = [1 - (r_2/r_1)]^3 \qquad k = [1 - (r_2/r_1)]^7 \qquad h/k = [1 - (r_2/r_1)]^{-4}. \tag{29}$$

For the extreme cylindrical case, from the Slieker expressions of h and k for small values of r_2/r_1, it is easy to obtain in the limit $(r_2/r_1) \rightarrow 0$ that

$$h = 45\,[\ln(r_2/r_1)]^{-2}/16 \qquad k = 1575\,[\ln(r_2/r_1)]^{-2}/512 \qquad h/k = 32/35. \tag{30}$$

For light-heated units, the extreme cylindrical case corresponds to the situation where an extremely fine hot wire is replaced by a very narrow light beam. In both cases, almost all of the fluid mixture remains at the temperature T_1 of the cold wall, whereas only a small region of the fluid close to the symmetry axis is heated. It is obvious that the thermal fields are the same in both cases, and, consequently, the convection patterns are also identical. This fact ensures that equation (30) can be used to describe the extreme cylindrical case in LH units by simply replacing (r_2/r_1) by the corresponding variable $\sqrt{2}\,\sigma/r_1$. The numerical results confirm this conclusion.

In LH units, there is not a situation equivalent to the *plane case*. However, there exists another limit case that corresponds to the fluid being heated by means of a largely expanded light beam, i.e. $x_0 \simeq 0$. As has been referred to above, the lowest order of approximation for $x_0 \simeq 0$ leads to a temperature profile linear in x,

$$T - T_1 = \Delta T(1 - x/x_0). \tag{31}$$

Calculations of the shape factors for this temperature field can be easily performed analytically, although details will not be given here for the sake of brevity. The final results for $x_0 \simeq 0$ are

$$h = 5/8 \qquad k = 21/32 \qquad h/k = 20/21. \tag{32}$$

As can be seen in figure 2, these results hold approximately for $\sqrt{2}\,\sigma/r_1 \geqslant 1$.

8. Discussion

The high insensitivity of the h/k quantity to the light beam width is surprising (the maximum deviation is lower than 5% in all the x_0 range). This means that the steady separation is largely independent of the temperature profiles in the tube. From a technical point of view, this result offers some clear experimental advantages, as regards the precision of the measured separation data. Although discussions on the power consumption of these units are not relevant here, it can however be noticed from equation (7) that large σ values will demand in practice correspondingly high power inputs in order to maintain a fixed ΔT value.

Figure 3 makes it evident that h/k values for CT units with quasi-plane geometry are larger than the LH ones, which are always close to unity. However, the additional dependence of the steady separation on r_1^{-4} makes the performances of LH configurations comparable to the standard ones. In fact, equations (26) and (28) together with equations (29) and (30) show that, for example, a small-size LH column with $r_1 = 1$ mm and $L =$ 250 mm has steady-state separations and relaxation times similar to a conventional CT quasi-plane column of the same length and an annular gap width of $w = 1$ mm. This result added to the constructional and operational advantages of such simple LH units shows that this heating mode can convert thermogravitation into an attractive method to determine diffusion properties in liquid mixtures.

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