64. *Diffusional Band Spreading in Gas-chromatographic Columns. Part I. The Elution of Unsorbed Gases.*

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It has been shown that diffusion coefficients can be measured reasonably accurately from elution curves, and that the labyrinth constant for packed columns, γ, is probably unity. The eddy diffusion contribution to the plate height cannot be measured reliably, but probably lies between one and two support-particle diameters.

The rate theory of chromatography as presented by van Deemter, Zuiderweg, and Klinkenberg[1] has formed the basis of most studies of column performance. In its simplest form their equation reads

$$H = A + B/u + Cu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where H is the height equivalent to a theoretical plate, u is the carrier-fluid velocity, $A = 2\lambda d_p$, λ being an eddy diffusion constant, and d_p the support-particle diameter, $B = 2\gamma D_g$; γ is called the labyrinth factor, and D_g is the interdiffusion coefficient of the solute in the mobile (gas) phase; C is a coefficient relating to the rate of mass transfer in the sorbent phase.

In several investigations carried out to test this equation, the results generally fit an equation of this type, but the individual terms are rarely concordant. For example, some of the earlier results[1,2] indicated that λ increased with decreasing particle diameter, being as high as 8 for a column packed with Celite of $d_p \sim 30$ μ. Glueckauf,[4] however, found λ

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[1] van Deemter, Zuiderweg, and Klinkenberg, *Chem. Eng. Sci.*, 1956, **5**, 271.

[2] Keulemans and Kwantes, in " Vapour Phase Chromatography (report of symposium), 1957," ed. Desty, Butterworths, London, p. 15.

[3] Desty, Godfrey, and Harbourn, in " Gas Chromatography (report of symposium), 1958, " ed. Desty, Butterworths, London, p. 200.

[4] Glueckauf, in ref. 3, p. 33.

to be about unity, and values between 0·3 and 1·5 may be inferred from other work.[3-6] It has also been suggested [5,7,8] that λ may be zero or effectively so. Values obtained for B indicate [1-5,7,9] that γ lies between about 0·5 and 1, and the present authors [5] found evidence which suggested that $B = k_1 + k_2d_p$, k_1 and k_2 being constants. The apparent conflict seems most likely to arise from inaccuracies in the determination of H, incorrect interpretation and evaluation of u, the use of insufficiently wide ranges of velocities, the use of graphical methods in the calculation of A, B, and C, and, finally, the approximate nature of equation (1). In the work described here every effort has been made to eliminate errors arising from these sources. The experiments designed to evaluate λ and γ involved a comparison of the elution of unsorbed gases from both open tubes and packed columns. Further, cognisance was taken of the need to introduce a coefficient C_g relating to mass-transfer effects in the gas phase as indicated by Golay [10] and van Deemter,[11] and also that B and C_g were pressure-dependent. Extending equation (1) we have

$$H = A + B/u + (C_g + C_l)u \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where C_l is the liquid mass-transfer coefficient. The appropriate velocity is that corrected for the compressibility of the carrier gas by use of James and Martin's correction factor f; [12] thus $u = u_0f$, where u_0 is the carrier-gas velocity measured at the column outlet pressure. However, it has been shown [8] that $B = B_0f$, and because of the inverse relation of C_g to D_g, presumably, $C_g = C_g^0/f$, B_0 and C_g^0 being values again corresponding to the outlet pressure. In order to standardise B and C, they may be converted into their values at 1 atm. pressure, B' and C_g', and then

$$H = A + B'/p_0u_0 + C_g'p_0u_0 + C_lu_0f \quad . \quad . \quad . \quad . \quad . \quad (3)$$

p_0 being the column outlet pressure (in atm.). However, $p_0u_0 = u'$, the gas velocity corresponding to unit outlet pressure, hence

$$H = A + B'/u' + C_g'u' + C_lu'f/p_0 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

For our present purposes, since the work is associated with the elution of unsorbed materials, the last term vanishes and the relevant equation for further discussion is

$$H = A + B'/u' + C_g'u' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

EXPERIMENTAL

Gas samples were added to the carrier-gas stream by means of the stainless-steel rotary valve described below. They then passed through one side of a twin-cell katharometer before entering the chromatographic column. Thus, an " injection peak " was recorded and so both the initial volume occupied by the sample and the time of sample introduction could be accurately determined. The other cell of the katharometer was used to monitor the column effluent. The carrier gas was oxygen-free nitrogen from a cylinder. Throughout the experiments the columns were kept at 51° in a forced-convection air-thermostat.

Sample-injection System.—Many methods of and devices for injecting samples into the carrier-gas stream were tried, but were all found to be unsatisfactory for the projected experiments. So a new type was devised (see Fig. 1). The multiple on-off, isolating action derives

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[5] Bohemen and Purnell, in ref. 3, p. 6.
[6] Scott, in ref. 3, p. 189.
[7] Littlewood, in ref. 3, p. 23.
[8] Brennan and Kemball, *J. Inst. Petroleum*, 1958, **44**, 14.
[9] Rijnders, in ref. 3, p. 18.
[10] Golay, in ref. 3, p. 36.
[11] van Deemter, Informal Symposium, Gas Chromatography Discussion Group, Cambridge, Oct. 4th, 1957.
[12] James and Martin, *Biochem. J.*, 1952, **50**, 679.

from a set of sloping O rings. With the valve in the position shown in the diagram the carrier gas entered port 1, went through the valve between barrel and key, and then left by port 2, which was connected to the katharometer with 1·4 mm. internal-diameter stainless-steel tubing. A 1 ml. volume stainless-steel by-pass, to which a modified petrol union containing a serum cap was hard-soldered so as to enable syringe injection of samples, was connected across ports 3 and 4. All connections to the ports of the rotary valve were made by means of the O ring connector also illustrated in Fig. 1. Samples of the permanent gases after introduction into the by-pass were then swept into the carrier-gas stream by rotating the inner cylinder of the valve through 180°.

Construction of Columns.—Columns were packed in stainless-steel tubing of measured length and diameter, the columns, in each case, being packed after the tubes had been bent into a U-shape. All the columns containing Sil-O-Cel firebrick contained also polyethylene glycol 400, which had been distributed on the brick by deposition from a solution in acetone.

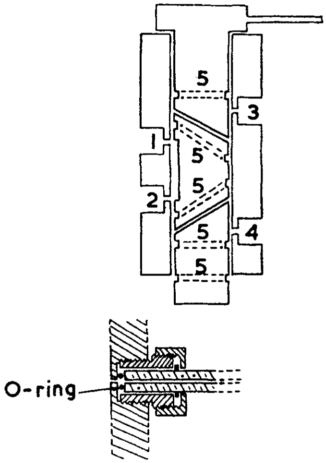

FIG. 1. *Sampling valve and* O *ring connectors.* 1, *Carrier-gas entry*; 2, *outlet to column*; 3 *and* 4, *by-pass volume*; 5, *isolating* O *rings.*

The prepared material, after being heated under a vacuum, was poured into the stainless-steel tube and packed down by tapping the column. Initially, the decrease in the volume occupied by the packing was rapid but, after about 10 min., the rate of volume change became substantially constant. Study revealed that this steady decrease was due to break-up of the solid particles, and hence the packing procedure was discontinued when this stage was reached.

The long columns containing glass beads were packed by passing nitrogen through the column and tapping as before. The packing density was found to be practically independent of the column length.

Determination of Column Efficiencies.—The number of theoretical plates, N, associated with any solute eluted from a column was determined by use of Glueckauf's equation [13] $N = 8(l/w_e)^2$ where w_e is the width of the elution curve at the $(1/e)$th height and l is the distance between the point of injection and the peak maximum. The method of evaluating N which was suggested at the 1956 London Symposium was not adopted, since it was impossible to draw tangents at the points of inflection of narrow elution curves accurately.

The moment of sample injection was accurately known from the " injection " peak. When peaks emerged rapidly from the column the chart speed was increased suitably; the maximum speed available with the 1 mv Honeywell–Brown recorder used in this work was 120″ per hour. The chart speed was checked at frequent intervals and was found to be constant although about $\frac{1}{2}$% less than was specified. l and w_e were generally measured with a travelling microscope.

RESULTS AND DISCUSSION

Permeability to Gas Flow.—The measurement of column permeability provides an independent method for determining the mean size of the particles of packing. The gas

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[13] Glueckauf, *Trans. Faraday Soc.*, 1955, **51**, 34.

velocity at the column outlet, u_0, defined by $u_0 = F_0/A\varepsilon$, where F_0 is the volume flow rate measured at the column temperature and outlet p_0, A is the cross-sectional area of the containing tube, and ε is the porosity, is related to column parameters by $u_0 = B_0(p_i^2 - p_0^2)/2\eta\varepsilon L p_0$, p_i being the column inlet pressure, L the column length, η the viscosity coefficient, and B_0 the specific permeability coefficient. By plotting u_0 against $[(p_i^2 - p_0^2)/p_0]$, B_0 can be evaluated if L, η, and ε are known or measured. The value of η used here ($1{\cdot}91 \times 10^{-4}$ g. cm.$^{-1}$ sec.$^{-1}$) was calculated from the equation quoted by Moelwyn-Hughes,[14] while ε was measured by use of the equation $\varepsilon = 1 - m\rho_b/V_c$, wherein, for Sil-O-Cel, ρ_b is the particle density measured under mercury (bulk density), while for glass beads it represents the true density; m is the mass of packing and V_c is the total packed column volume.

According to the Kozeny–Carman equation [15]

$$B_0 = d_p{}^2\varepsilon^3/180(1 - \varepsilon)^2$$

where d_p is the diameter of a sphere with the same specific surface as the particles in the bed. Some values of ε and of d_p derived from evaluations of B_0 for some firebrick and glass bead columns are listed in Table 1. Included for the former are surface areas per gram of solid, S, calculated from $S = 0{\cdot}75(1 - \varepsilon)V_c/d_p$, values of d_p derived from B_0 again being used.

TABLE 1.

Firebrick

Column	Length (cm.)	Sieve size (range) (mm.)	ε	d_p (mm.	Surface area (cm.^{2} g.$^{-1}$)
1	136	0·635—0·425	0·465	0·32	258
2	131	0·254—0·211	0·444	0·16	516
3	120	0·127—0·084	0·391	0·10	825

Glass beads

Column	Length (cm.)	Manufacturer's quoted size (mm.)	ε	d_p (mm.
4	100	0·11	0·377	0·088
5	99	0·10	0·359	0·080
6	376	0·10	0·365	0·079
7	378	0·3—0·4	0·370	0·376

The derived values of d_p for the glass-bead columns 4 and 5 are somewhat lower than the manufacturer's quotation, but are in the same ratio. Columns 5 and 6, constructed of the same beads, differed considerably in length but gave the same result for d_p, while 6 and 7, constructed of beads of different diameter, operated under pressure gradients differing by a factor of nearly twenty. The results obtained are, therefore, sufficiently good to substantiate the experimental procedure employed and to validate the extension of the method to the Sil-O-Cel columns. The considerable discrepancy between the listed values of d_p and the sieve grades for the coarser Sil-O-Cel particles can, therefore, be taken to show that sieve sizes are unreliable as a means of determining d_p. In any event, the particle diameter used in the original derivation of equation (1) was that defined by the permeability equation, and so is the one appropriate to the discussion of the dependence of the column efficiency on support particle size.

The results listed in Table 1 for the Sil-O-Cel columns show conclusively that resistance to gas flow arises from the external surface of the particles only. The largest Sil-O-Cel surface area measured, *e.g.*, that for column 3, is only 825 cm.^{2} g.$^{-1}$, in contrast to the value of 3×10^4 cm.^{2} g.$^{-1}$ found from adsorption measurements.[16] These and the earlier results show that the Kozeny–Carman equation is applicable to the flow of gas through

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[14] Moelwyn-Hughes, " Physical Chemistry," Pergamon Press, London, p. 597.

[15] Carman, " The Flow of Gases through Porous Media," Butterworths, London, p. 8.

[16] Bohemen, Langer, Perrett, and Purnell, *J.*, 1960, 2444.

chromatographic columns, and also that this flow does not involve the internal volume of the particles.

Retention Volume of Unsorbed Gases.—The retention volume, V_d, of hydrogen and carbon dioxide eluted in nitrogen from columns 1—7 are listed in Table 2, which includes also the interparticle (void) volumes V_v, the intraparticle (pore) volumns V_p, and their sums. The retention volumes were measured integrally and each is the mean of 25—50 measurements. The results in the Table represent altogether more than 300 measurements.

TABLE 2.

Column	V_p	V_v	$(V_p + V_v)$	V_d (H_2)	V_d (CO_2)
1	5·5	9·6	15·1	16·1	18·0
2	5·5	8·7	14·2	15·0	17·0
3	5·5	7·0	12·5	13·8	15·7
4	—	5·7	5·7	5·8	—
5	—	5·4	5·4	5·7	—
6	—	21·0	21·0	21·4	—
7	—	21·4	21·4	21·8	—

As would be expected, the retention volume of hydrogen eluted from glass-bead columns corresponds closely to the void volume. With Sil-O-Cel columns, however, the retention volumes are about twice the void volume and close to the sum $(V_v + V_p)$, that is, the total column free-gas volume. Similar findings have been described by Primavesi.[17] The slight discrepancies are greater than the errors involved in the measurements and so are probably due to unavoidable sorption, a view which is supported by the greater retention of carbon dioxide than of hydrogen. Since it has already been shown that carrier-gas flow occurs between the particles only, the equivalence of V_d and $(V_p + V_v)$ requires explanation. This is as follows.

Consider a single theoretical plate in a column containing only a porous non-sorbing solid. The total gas space is divided into a mobile volume ΔV_v and a static volume ΔV_p. If a sample of some gas is injected into the static carrier gas already in this plate it will be uniformly distributed through both ΔV_v and ΔV_p. Addition to the plate now of a volume ΔV_v of carrier gas carries the original contents of the plate void volume on into the next plate, but leaves the contents of the pore volume behind. The latter then equilibrate throughout the total gas space. Continued addition of carrier thus leads to a partitional spreading of the initial, injected gas packet, and the process is effectively gas–gas chromatography. The necessary " immiscibility " of phases arises from the relative motions of the two gas regions. Thus, the conventional chromatographic retention volume equation can be applied, and $V_d = V_v + KV_p$. However, since gases are miscible in all proportions, the partition coefficient K is always unity, *i.e.*, at equilibrium the concentrations in ΔV_v and ΔV_p are identical, and hence $V_d = V_v + V_p$, as found. That the equilibration process involved is virtually instantaneous follows from the fact that it is ignored in column theory. More important, the process must precede all other partitional mechanisms in packed columns and since the partition coefficients determined by gas–liquid chromatography commonly agree well with those found by static methods, it must therefore occur very rapidly indeed.

These results and the explanation offered are important, since they establish that the retention volume of an unsorbed gas does not measure the void volume alone if the solid support is porous. Thus, it is correct to calculate the capacity factor k of the van Deemter and the Golay theory from the ratio $(V_R' - V_d)/V_d$, where V_R' is the apparent retention volume of some sorbed substance and V_d is that of an unsorbed material. Further, partition coefficients calculated from $(V_R' - V_d) = KV_l$, where V_l is the volume of stationary phase, are not subject to error. However, it is incorrect to calculate carrier-gas velocities for use in theoretical studies from the retention times of unsorbed substances (air). These must be evaluated from volume flow and porosity data. If they are not, then, for example, values of B derived from application of equation (1) to the results will be too small by about a factor of 2, while C will be correspondingly too great. This

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[17] Primavesi, Informal Symposium, Gas Chromatography Discussion Group, Bristol, Sept. 25th, 1959.

might explain some of the low values of γ in the literature. It might be thought that the contribution of a longitudinal diffusional band spreading to the theoretical plate height would be determined by the total time spent in the column, but, in fact, the process only contributes to H during the time spent by the material in the void volume because d_p must, according to theory, be smaller than H. Thus, within the particle there must be uniformity of concentration, and spreading from plate to plate can only occur in the void volume.

Diffusion Coefficients from Elution Data for Open Tubes.—For elution from an open tube, equation (5) reduces to

$$H = 2D_g'/u' + C_g'u' \qquad (6)$$

In the conditions of the present experiments the contribution of the second term in (6) to the value of H never exceeded 3%, hence, to a reasonable approximation,

$$H = 2D_g'/u' \qquad (7)$$

Table 3 lists values of D_g' derived through equation (7) and also the corresponding literature values for hydrogen,[18] oxygen,[18] and carbon dioxide [19] in nitrogen at 51°. Also included for the last two are D_g' values deduced through (6), which show that C_g' may, in fact, be neglected in subsequent discussion. The appropriate values of C_g' were calculated from Golay's equation [10] $C_g' = r_0^2/24D_g'$, wherein r_0 is the tube radius.

TABLE 3. *Interdiffusion coefficients: some permanent gases in nitrogen at* 1 *atm. pressure and* 51°.

Gas	u' (cm. sec.$^{-1}$)	D_g' (cm.^{2} sec.$^{-1}$)	D_g' (6) (cm.^{2} sec.$^{-1}$)	D_g' (lit.) (cm.^{2} sec.$^{-1}$)
Hydrogen	0·85	0·876	—	
	1·28	0·881	—	0·909
	1·56	0·919	—	
Oxygen	0·72	0·260	0·258	0·244
	1·42	0·267	0·261	
Carbon dioxide	0·73	0·188	0·186	0·194

The agreement between the chromatographic values and those in the literature is good, the greatest discrepancy being about 7%. The chromatographic values increase slightly with increased velocity, a feature which to some extent, but not completely, is remedied by use of equation (6). The method is evidently suited to the determination of diffusion coefficients, and the findings provide a basis for the extension of equation (6) to packed columns.

Diffusion Coefficients from Elution Data for Packed Columns.—For unsorbed gases in packed columns operated at low velocity the basic equation (5) reduces to

$$H = A + B'/u' \qquad (8)$$

A plot of H against $1/u'$ should be linear, of slope $2\gamma D_g'$ and intercept A. Plots of this type were used by Glueckauf [4] in connection with frontal technique studies. Fig. 2 shows such plots obtained in this work for the elution of both hydrogen and carbon dioxide in nitrogen at 51° from a Sil-O-Cel column of $d_p = 0{\cdot}01$ cm. Both sets of figures give straight lines and the fit of all points, which represent an average of at least three measurements, is excellent. Even so, the intercepts for the two gases differ by 50%. This illustrates the extreme difficulty of evaluating A with any certainty by graphical methods.

An alternative procedure is to evaluate A and B' by a method of successive approximation using equation (8). Values found in this way for columns 1, 2, and 3 and also calculated values of λ and γ are contained in Table 4, representing about 30 measurements with each column extending over the carrier-gas velocity range 1—10 cm. sec.$^{-1}$ for hydrogen and 1—5 cm. sec.$^{-1}$ for carbon dioxide elution. The values of A listed are not

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[18] Internat. Critical Tables, Vol. V, p. 62.

[19] Boardman and Wild, *Proc. Roy. Soc.*, 1937, *A*, **162**, 511.

TABLE 4.

	Hydrogen				Carbon dioxide			
Column	A (cm.)	λ	B' (cm.^{2} sec.$^{-1}$)	$B'/2D_g' = \gamma$	A (cm.)	λ	B' (cm.^{2} sec.$^{-1}$)	$B'/2D_g' = \gamma$
1	0·030	0·5	1·72	0·95	0·039	0·6	0·335	0·86
2	0·025	0·8	1·85	1·02	0·024	0·7	0·380	0·98
3	0·030	1·5	1·75	0·96	0·023	1·2	0·344	0·89

considered to be more accurate than ±0·005, but values of B' are probably good to ±0·02 for hydrogen and ±0·01 for carbon dioxide. The combined values of A and B' in each case reproduce the experimental data to better than 3% over the whole range of velocities.

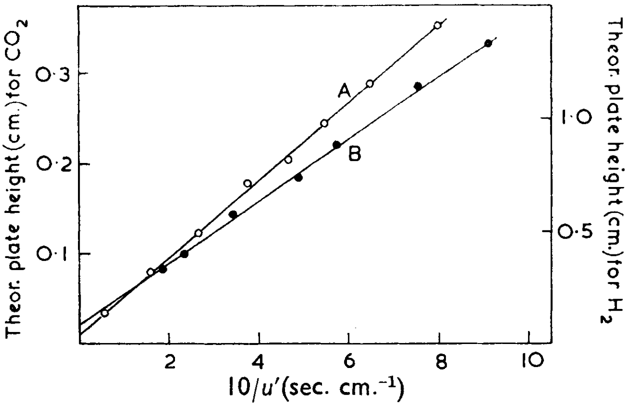

FIG. 2. *Dependence of H upon $1/u'$ in the elution of* (A) *hydrogen and* (B) *carbon dioxide in nitrogen at* 51° *from Sil-O-Cel column of d_p =* 0·010 *cm.*

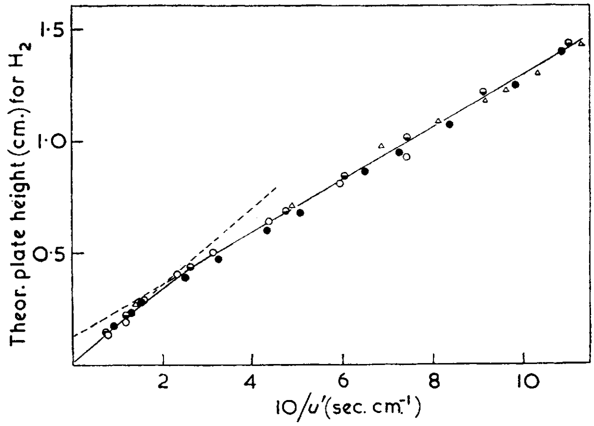

FIG. 3. *Dependence of H upon $1/u'$ in the elution of hydrogen in nitrogen at* 51° *from four glass-bead columns.*
Column nos.: ○ 4; △ 5; ◒ 6; ● 7.

The values of λ agree reasonably for the two gases and apparently increase with decreasing d_p in such a way as to keep A roughly constant. However, the variation is comparable to the probable accuracy of the measurements, and so λ may be independent of d_p. The only safe conclusion is that λ probably lies between 0·5 and 1.

The average value of γ is 0·94, which is the highest yet recorded and may result from the method used here to calculate the carrier-gas velocity. Had the air peak retention time been used for the latter purpose, a mean γ of 0·60 would have been obtained. There is no obvious trend of γ with changing d_p, although γ is high when A is low. This might mean that the variations in γ are associated with exaggerated estimates of A.

Fig. 3 shows data for the elution of hydrogen in nitrogen, at 51°, from the four columns of glass beads (4—7). The dependence of H upon $1/u'$ is seen to be independent of column length, and the pressure correction method for the velocity is verified, since the pressure drop across columns 6 and 7, at a given velocity, differed by as much as a factor of 18. In addition, H is virtually independent of d_p, as would be expected if A were very small. An unexpected feature of the results is that in the range $1/u' = 0$—2 sec. cm.$^{-1}$, the derived values of γ agree with those determined for Sil-O-Cel columns. At higher values of $1/u'$, however, γ appears to be about 0·6, in accord with the findings of earlier workers.[4,7] The values of A obtained by extrapolation of the low-velocity data are obviously of little significance since lower values of H are achieved in practice at high velocities. The reason for the change of slope of the graph, which was not observed with the packed columns, is unknown. The effects observed on going towards higher velocities are the opposite of those to be expected if some gas mass-transfer mechanism is operative. It may thus be that the anomaly is associated with localised gas-flow irregularities which depend upon the smoothness or roughness of the particles in the bed.

The conclusions to be drawn from this work are that while B' and, hence, D_g', may be reasonably accurately determined from chromatographic data through the van Deemter equation, it is not possible, even with extreme experimental precautions, to make an unequivocal estimate of the magnitude of A. However, it seems established that λ never significantly exceeds unity, and so eddy diffusion is not, here at least, a limiting factor in the attainment of high column efficiencies.

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