Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Buys, T. S. , Smuts, T. W. and De Clerk, K.(1975) 'Optimization Theory of Preparative Production Rate in Open Tubular Gas Chromatography', Separation Science and Technology, 10: 4, 471 — 487
To link to this Article: DOI: 10.1080/00372367508058034
URL: http://dx.doi.org/10.1080/00372367508058034

SEPARATION SCIENCE, 10(4), pp. 471–487, 1975

Optimization Theory of Preparative Production Rate in Open Tubular Gas Chromatography

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Abstract

Optimization theory is used to define operating conditions for the production rate in open tubular gas chromatography for a variety of practical constraints.

INTRODUCTION

The basic equations relating production rate to operating parameters in preparative chromatography have been formulated in a previous paper (*1*). In the present study these equations are applied to the specific case of open tubular columns. The choice of open columns as a starting point is in part motivated by the fact that the column processes are well understood. It is, however, not merely an application of academic interest despite the inherent low capacity of such columns. On the contrary, a considerable segment of preparative work in chromatography is expected to be concerned with difficult separations of rare substances at relatively low yield, where the high resolution of open columns could be used to advantage.

It should again be emphasized that the choice of production rate as the object of study does not imply that it is regarded as synonymous with

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preparative efficiency since a variety of factors can determine the relative importance of time, yield, cost, etc. Justification for its choice stems from the belief that most overall criteria will have a significant functional dependence on the rate.

THEORY

The expression for production rate E_p, based on the simplifying assumptions outlined in Ref. *1*, is given by

$$E_p = C_i F \,\mathrm{Re}\, r_c \left(1 - \frac{G_1 H}{l}\right)^{1/2} \tag{1}$$

where

$$F = \frac{2^{1/2}\pi^{3/2} v_m (1-\theta)[1 + \mathrm{erf}(2^{1/2}R)]}{48R} \tag{2}$$

$$G_1 = \left[\frac{4(1+k)R}{k(\alpha - 1)}\right]^2 \tag{3}$$

$$k = K\frac{\theta(2-\theta)}{(1-\theta)^2} \tag{4}$$

For laminar flow in open columns

$$H = \frac{Br_c}{\mathrm{Re}} + C\,\mathrm{Re}\,r_c \tag{5}$$

with

$$B = \frac{4(1-\theta)}{\mathrm{Scm}} \tag{6}$$

$$C = C_m + C_s \tag{7}$$

$$C_m = \frac{(1 + 6k + 11k^2)}{24(1+k)^2}\frac{\mathrm{Scm}}{2(1-\theta)} \tag{8}$$

$$C_s = \frac{1}{12}\frac{k}{(1+k)^2}\frac{\theta^2(2-\theta)^2}{(1-\theta)^5}\frac{v_m}{v_s}\mathrm{Scs} \tag{9}$$

The plate height expression is written in terms of the Reynolds number Re to facilitate recognition of the turbulent flow region.

Production rate is thus seen to be a function of the variables θ, Re, r_c, l, α, K, k, v_m, v_s, Scm, Scs, P_0, μ_m, and R. The inlet volume V_i has already been eliminated as a dependent variable and is given by

$$V_i = \pi(2\pi)^{1/2}(1 + k)r_c^2 \frac{(1 - \theta)^2 l}{G_1^{1/2}} \left[1 - \frac{G_1 H}{l}\right]^{1/2} \tag{10}$$

Of the variables mentioned above, all except the first five can be regarded as parameters with values fixed at representative levels. E_p can then be formally interpreted as a hypersurface in 6-dimensional space. A point on this surface corresponds to a uniquely defined experimental arrangement. However, not all points on the surface are in reality accessible since they also necessarily have to conform to the equation relating pressure gradient to flow. In this case it is the Poisseuille equation

$$r_c^3 = \frac{8\mu_m v_m p l}{(1 - \theta)^3 (p^2 - 1) P_0} \mathrm{Re} \tag{11}$$

The intersection between the E_p surface and that defined by Eq. (11) defines a 5-dimensional hypersurface. This surface is unique but can be functionally described in five different but equivalent ways depending on which variable in E_p is eliminated by means of Eq. (11). This is summarized in Table 1.

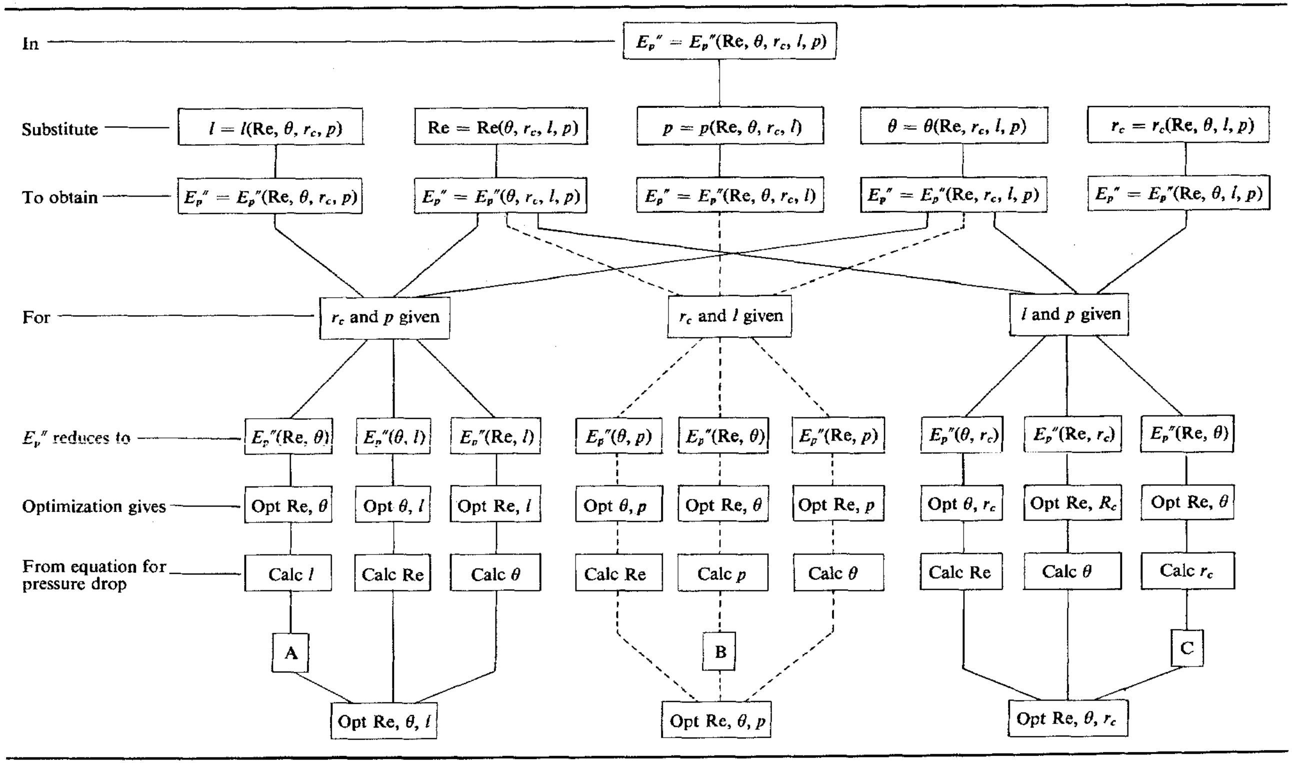
The information content of the 5-dimensional surface is still excessive for representation. It is convenient to select only those regions which correspond to a maximum in E_p by differentiating E_p with respect to those variables which exhibit optima and equating the result to zero. The resulting equations can define different hypersurfaces for the nine situations depicted in Table 1 so that the intersections to which the system point is constrained may also differ. Each of these situations corresponds to a specific experimental arrangement, viz., that in which the same set of variables which are held constant during partial differentiation are also kept constant during the experiment. An important practical implication is that the variable which is eliminated from E_p becomes a dependent variable, the value of which will have to be adjusted to conform with the optimized value of the variable with respect to which the optimization is carried out. The present study is devoted to an analysis of three of the cases which are regarded as of importance in practice, viz.:

(A) r_c and p given, l dependent.
(B) r_c and l given, p dependent.
(C) l and p given, r_c dependent.

The results of a general analysis of these three situations are tabulated

TABLE I

Classification of Optimization Procedures



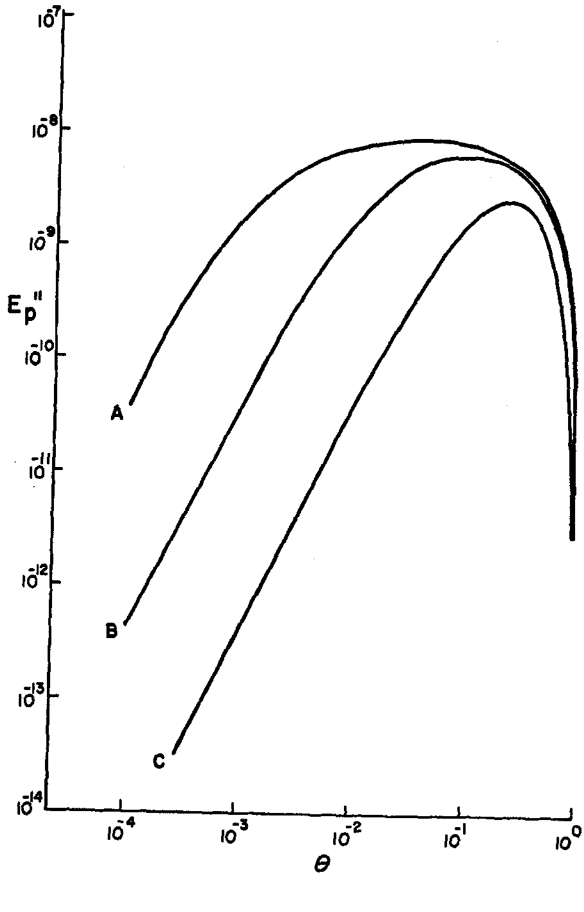


FIG. 1. Determination of θ_{opt} for gas–liquid chromatography in open tubular columns. $\nu_m = 2.0 \times 10^{-5}$ m^2/sec, $\nu_s = 1 \times 10^{-4}$ m^2/sec, $\mu_m = 2.0 \times 10^{-5}$ Pa.s, Scm = 1, Scs = 1000, $R = 1.5$ E_p'' in m^3/sec.

below, but the detailed numerical results will be confined to Case B. Two aspects common to all will, however, be dealt with first. These are the validity of neglecting the B term in the plate-height equation and the optimization with respect to θ.

Neglect of B Term

A qualitative inspection of the basic equation suggests that the effect of the B term in the H-expression at optimum flow velocity should be relatively slight. If B could therefore be set equal to zero at the outset, this would not only substantially simplify the mathematics, but in so doing would also serve to accentuate the dominating features in the interpretation of the results. Criteria for the validity of the neglect of B are developed in Appendix 1 for the Case B. It is shown there that the ratio of the true optimum in Re, Re^t(opt), to the approximate optimum, Re (opt), is better than 0.95 provided that $l > 2l_a$. (For details see Fig. A1.) l_a is the minimum column length at which the specified resolution is achieved for zero yield:

$$l_a = 2G_1(BC)^{1/2}r_c \tag{12}$$

The mathematics for the other two cases is involved and analytical solutions were not found. The results are not expected to differ significantly from the above, however, and B will in the rest of the analysis be neglected on the proviso of a suitable l' ratio.

θ Optimization

If B is neglected, it is shown in Appendix 2 that the optimum in θ is a function only of K for given Scm, Scs, v_m, and v_s. The results of a numerical optimization of E_p with respect to θ is depicted in Fig. 1. Inspection of this figure shows that: (a) The optimum θ decreases slightly with increasing K (from $\theta_{opt} \approx 0.06$ for $K = 1$ to $\theta_{opt} \approx 0.03$ for $K = 100$). (b) The position of the optimum becomes less critical with increasing K. (c) Production rate at optimum θ increases with increasing K.

Unfortunately, θ optimization will not always be realizable in practice since the thickness of the stationary phase is restricted to a maximum of about 2×10^{-6} m (*2*) before instability sets in. The calculations were nevertheless carried through for both the θ_{opt} and θ_{cr} values restricted by the constraint $d_f = 2.5 \times 10^{-6}$ m. This was considered worthwhile in order to provide a comparative basis relative to which the merits of artifically increasing d_f could be assessed.

TABLE 2

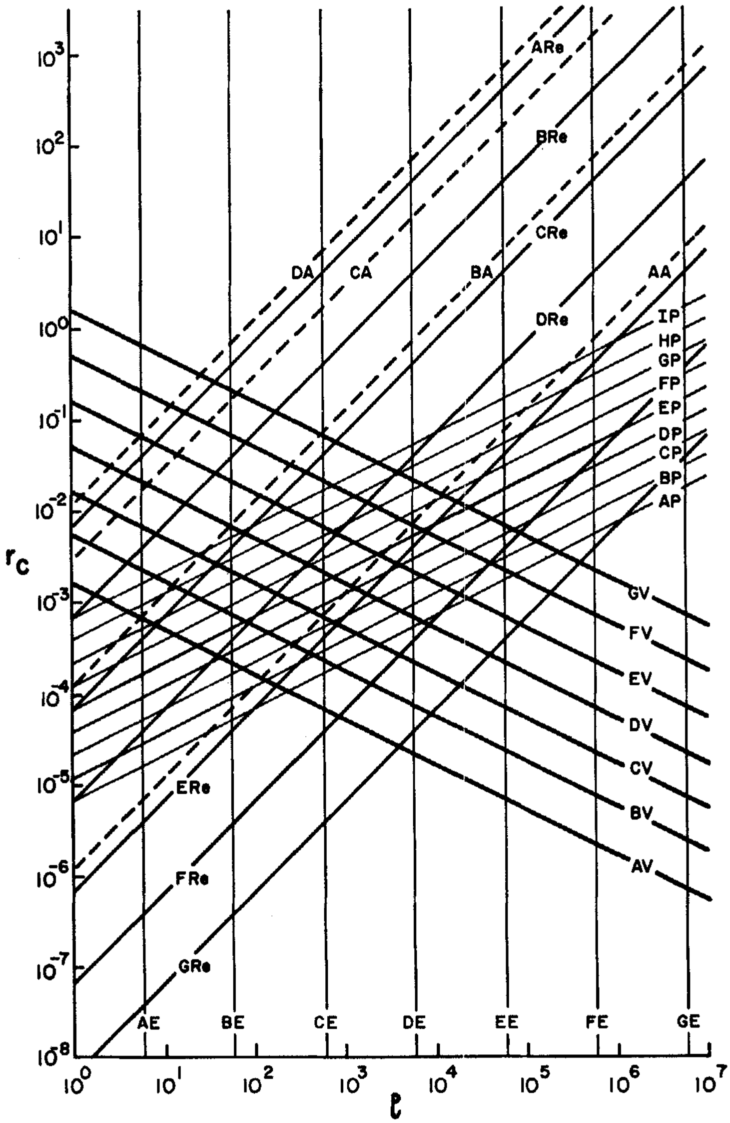
Results of E_p Optimization

Optimum	r_c and p given (A, Table 1)	r_c and l given (B, Table 1)	l and p given (C, Table 1)
θ^a	0.026	0.026	0.026
Re	$\{r_c^2(\alpha - 1)^2/2G_0CQ_1^3\}^{1/2\ b}$	$2l(\alpha - 1)^2/3G_0Cr_c$	$\{2l^{2/3}(\alpha - 1)^2/3G_0CQ_1\}^{3/4}$
r_c	—	—	$\{2Q_1^3l^2(\alpha - 1)^2/3G_0C\}^{1/4}$
l	$\{2G_0Cr_c^4/Q_1^3(\alpha - 1)^2\}^{1/2}$	—	—
p	—	$PQ\{1 + [1 + 1/(PQ)^2]^{1/2}\}^c$	—
E_p[Re(opt)]	$C_lFr_c^2(\alpha - 1)/2(G_0CQ_1^3)^{1/2}$	$2C_lFl(\alpha - 1)^2/3^{3/2}G_0C$	$2C_lFl(\alpha - 1)^2/3^{3/2}G_0C$
V_l[Re(opt)]	$\pi(2\pi)^{1/2}(1 + k)r_c^4(1 - \theta)^2 \times C^{1/2}/Q_1^{3/2}$	$\pi(2\pi)^{1/2}(1 + k)r_c^2(1 - \theta)^2 \times(\alpha - 1)l/(3G_0)^{1/2}$	$2\pi^{3/2}(1 + k)Q_1^{3/2}(1 - \theta)^2 \times(\alpha - 1)^2l^2/3C^{1/2}G_0$

[a] θ (opt) determined graphically (Fig. 1).

[b] $Q_1^3 = \dfrac{8\mu_m v_m p}{(1 - \theta)^3(p^2 - 1)P_0}$.

[c] $PQ = 8\mu_m v_m l^2/3(1 - \theta)^3P_0G_1Cr_c^4$.



r_c
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
ARe
BRe
CRe
DRe
ERe
FRe
GRe
DA
CA
BA
AA
IP
HP
GP
FP
EP
DP
CP
BP
AP
GV
FV
EV
DV
CV
BV
AV
AE
BE
CE
DE
EE
FE
GE
10^0
10^1
10^2
10^3
10^4
10^5
10^6
10^7
ℓ

Optimization

In all three cases the optima could be found by standard differentiation, the details of which will not be reproduced here. The resulting expressions are summarized in Table 2, while the numerical results for Case B are represented in Figs. 2 and 3.

DISCUSSION

The graphs have been prepared in a manner which is standard procedure in the theory of optimization (e.g., Ref. *3*). All information is given in the form of families of contour lines representing the various constraints referred to a convenient base (in this case r_c, l). This type of representation is especially convenient since it reduces the information for a specific case to a single graph and allows the introduction of inequality constraints. These graphs can be applied in a variety of ways; the essential elements can be illustrated by means of a typical example.

The graphs were prepared for $K = 100$, but since E_p is relatively insensitive to K, the results can also be regarded as a first approximation for other K values. For a given α, the argument would proceed as follows.

(1) For $\alpha = 1.1$, say, the appropriate l_a line, viz., BA, divides the area into two regions of which only the one to the right of BA is accessible.

(2) Provided that $\theta = \theta_{\text{opt}} = 0.026$, the production rate is seen to be a linear function of the length l. For the present parameter values

$$E_p'' = \frac{E_p}{(\alpha - 1)^2 C_i} = \frac{2Fl}{3^{3/2} G_0 C} = 1.69 \times 10^{-7} l \tag{13}$$

FIG. 2. Representation of contours of the functions listed below on an r_c vs l frame of reference for $\theta = \theta_{\text{opt}} = 0.026$ and $K = 100$.

$E_p'' = E_p/(\alpha - 1)^2 C_i$: $AE - E_p'' = 10^{-6}$, $BE - E_p'' - 10^{-5}$, $CE - E_p'' = 10^{-4}$, $DE - E_p'' = 10^{-3}$, $EE - E_p'' = 10^{-2}$, $FE - E_p'' = 10^{-1}$, $GE - E_p'' = 10^0$ (m^3/sec).

$Re' = Re/(\alpha - 1)^2$: ARe $-$ Re$' = 10^1$, BRe $-$ Re$' = 10^2$, CRe $-$ Re$' = 10^3$, DRe $-$ Re$' = 10^4$, ERe $-$ Re$' = 10^5$, FRe $-$ Re$' = 10^6$, GRe $-$ Re$' = 10^7$.

$P' = p(\alpha - 1)^2/(p^2 - 1)$: $AP - P' = 10^{-6}$, $BP - P' = 10^{-5}$, $CP - P' = 10^{-4}$, $DP - P' = 10^{-3}$, $EP - P' = 10^{-2}$, $FP - P' = 10^{-1}$, $GP - P' = 10^0$, $HP - P' = 10^1$, $IP - P' = 10^2$.

$V_i' = V_i/(\alpha - 1)$: $AV - V_i' = 10^{-5}$, $BV - V_i' = 10^{-4}$, $CV - V_i' = 10^{-3}$, $DV - V_i' = 10^{-2}$, $EV - V_i' = 10^{-1}$, $FV - V_i' = 10^0$, $GV - V_i' = 10^1$ (m^3).
$l_a = 2G_0(BC)^{1/2} r_c/(\alpha - 1)^2$: $AA - \alpha = 1.01$, $BA - \alpha = 1.1$, $CA - \alpha = 1.5$, $DA - \alpha = 2$.

Other parameters as in Fig. 1

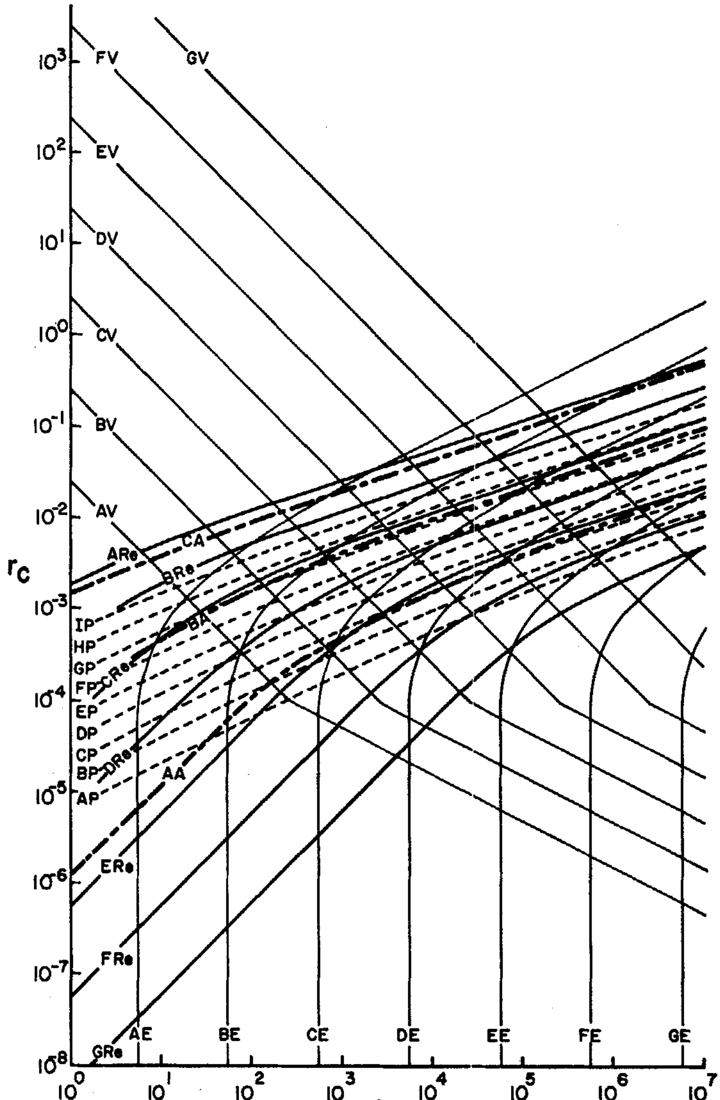


FIG. 3. Representation of contours of the functions listed below on an r_c vs l frame of reference for $d_f = 2.5 \times 10^{-6}$ m and K = 100 (the optimum θ was used for $r_c \leqslant d_f/\theta_{opt} \approx 10^{-4}$ m).

$E_p'' = E_p/(\alpha - 1)^2 C_i$; $\text{Re}' = \text{Re}/(\alpha - 1)^2$; $P' = p(\alpha - 1)^2/(p^2 - 1)$; and $V_i' = V_i/(\alpha - 1)$ as in Fig. 2.

$l_a = 2G_0(BC)^{1/2} r_c/(\alpha - 1)^2$: $AA - \alpha = 1.01$, $BA - \alpha = 1.1$, $CA - \alpha = 2$. Other parameters as in Fig. 1.

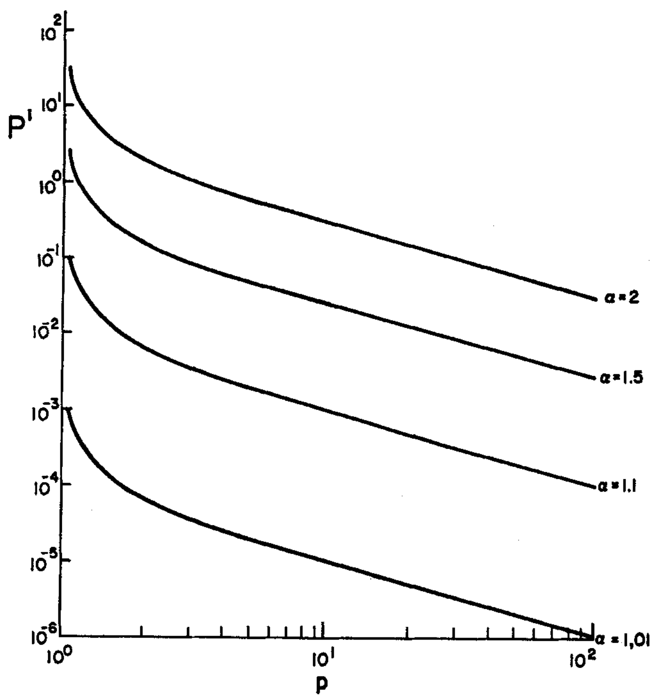


FIG. 4. Graphical representation of the pressure parameter $P' = p(\alpha - 1)^2/(p^2 - 1)$.

(for E_p in kg/sec, l in m, and C_i in kg/m^3). The price paid for increased production is thus solely dependent on the length l. When d_f is constrained to a maximum of $d_f = 2.5 \times 10^{-6}$ m, E_p also becomes dependent on r_c. This dependence causes E_p to decrease markedly with increasing r_c. Note, however, that in Fig. 3 the optimum θ was used for $r_c \leqslant d_f/\theta_{\text{opt}}$.

(3) For $\theta = \theta_{\text{opt}}$ the choice of E_p (and thus l, or vice versa) leaves one independent variable undetermined. This can be chosen from the group (r_c, p, Re, V_i), whereby the remaining variables are then uniquely determined. The choice of independent variable depends on which constraint is critical. Whatever the choice, however, the result can be interpreted as fixing the ratio between the inlet variance and that produced by the column as explained in a previous paper (*1*).

As an indication of theoretically possible operating conditions, the values of the system variables for a selection of lengths and α values at

TABLE 3

Possible Values of E_p ($r_c = 10^{-3}$ m, $K = 100$, $C_i = 1$ kg/m^3)[a]

α	l(m)					
	10^1		10^3		10^5	
	Optimum θ	$d_f = 2.5 \times 10^{-6}$ m	Optimum θ	$d_f = 2.5 \times 10^{-6}$ m	Optimum θ	$d_f = 2.5 \times 10^{-6}$ m
1.01	$l_a = 873.3 \gg l$ No production	$l_a = 3230 \gg l$ No production	$l_a = 873.3$ $p = 1.125$ $E_p = 1.69 \times 10^{-8}$ $V_i = 3.89 \times 10^{-5}$ Re = 6.88	$l_a = 3230 > l$ No production	$l_a = 873.3$ $p \gg 10^2$ (Impractical)	$l_a = 3{,}230$ $p \gg 10^2$ (Impractical)
1.1	$l_a = 8.7$ $p = 1.001$ $E_p = 1.69 \times 10^{-8}$ $V_i = 3.89 \times 10^{-6}$ Re = 6.88	$l_a = 32.3 > l$ No production	$l_a = 8.7$ $p = 23.57$ $E_p = 1.69 \times 10^{-6}$ $V_i = 3.89 \times 10^{-4}$ Re = 688.4	$l_a = 32.3$ $p = 10.56$ $E_p = 8.27 \times 10^{-7}$ $V_i = 3.78 \times 10^{-5}$ Re = 328.8	$l_a = 8.7$ $p \gg 10^2$ (Impractical)	$l_a = 32.3$ $p \gg 10^2$ (Impractical)

[a] l_a in m. E_p in kg/sec; to convert to kg/day, multiply by 8.64×10^4. V_i in m^3; to convert to cm^3, multiply by 1×10^6.

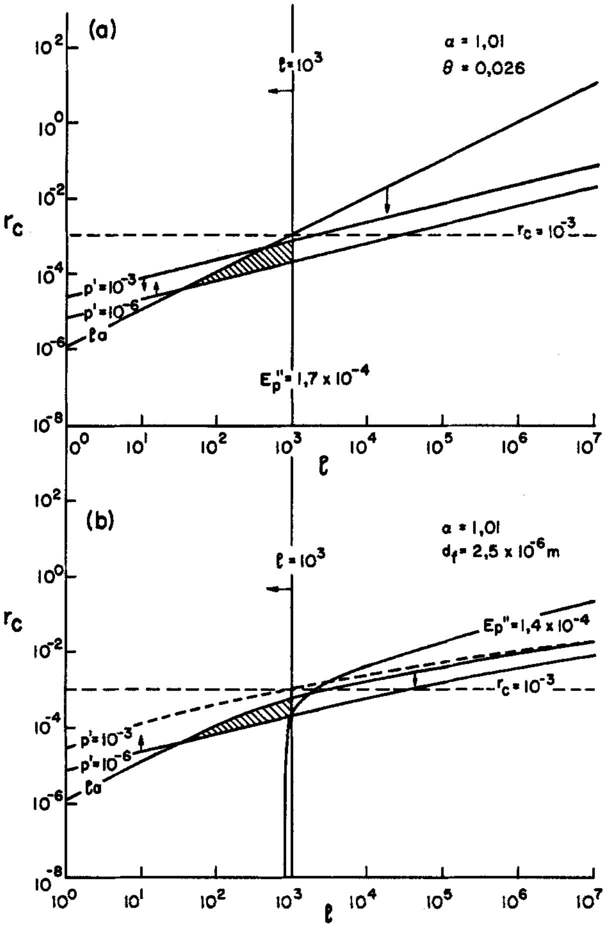


FIG. 5. Contour graphs to illustrate the use of inequality constraints on different variables. K = 100, other parameters as in Fig. 1.

$r_c = 10^{-3}$ m are given in Table 3. The use of inequality constraints is illustrated in Fig. 5 where the shaded area defines the accessible operating region.

APPENDIX 1

Evaluation of Neglect of B Term in Optimization

From Eq. (1)

$$E_p = C_l F \mathrm{Re} r_c \left(1 - \frac{G_1 H}{l}\right)^{1/2} \tag{A1}$$

The minimum length, l_a, at which production will start is given by

$$l_a = G_1 H_{\min} \tag{A2}$$

where $H_{\min}$ corresponds to the flow velocity $\mathrm{Re}^a(\mathrm{opt}) = (B/C)^{1/2}$ which minimizes the plate height, i.e.,

$$H_{\min} = 2(BC)^{1/2} r_c \tag{A3}$$

Substitution of Eq. (A3) in Eq. (A2) gives

$$l_a = 2G_1(BC)^{1/2} r_c \tag{A4}$$

which can be used to eliminate G_1 from Eq. (A1):

$$E_p = C_l F \mathrm{Re} r_c \left[1 - \frac{1}{2l'}\left(\frac{\mathrm{Re}^a(\mathrm{opt})}{\mathrm{Re}} + \frac{\mathrm{Re}}{\mathrm{Re}^a(\mathrm{opt})}\right)\right]^{1/2} \tag{A5}$$

Setting $(\partial E_p/\partial \mathrm{Re})_{l,r_c} = 0$ and solving for Re yields

$$\mathrm{Re}^t(\mathrm{opt}) = \frac{2}{3} l' \mathrm{Re}^a(\mathrm{opt}) \left\{1 + \left[1 - \frac{3}{4}\left(\frac{1}{l'}\right)^2\right]^{1/2}\right\} \tag{A6}$$

where B has been retained.

If B is neglected, one obtains similarly

$$\mathrm{Re}(\mathrm{opt}) = \tfrac{4}{3} l' \mathrm{Re}^a(\mathrm{opt}) \tag{A7}$$

so that

$$\frac{\mathrm{Re}^t(\mathrm{opt})}{\mathrm{Re}(\mathrm{opt})} = \frac{1}{2}\left\{1 + \left[1 - \frac{3}{4}\left(\frac{1}{l'}\right)^2\right]^{1/2}\right\} \tag{A8}$$

Equation (A8) is graphed in Fig. A1.

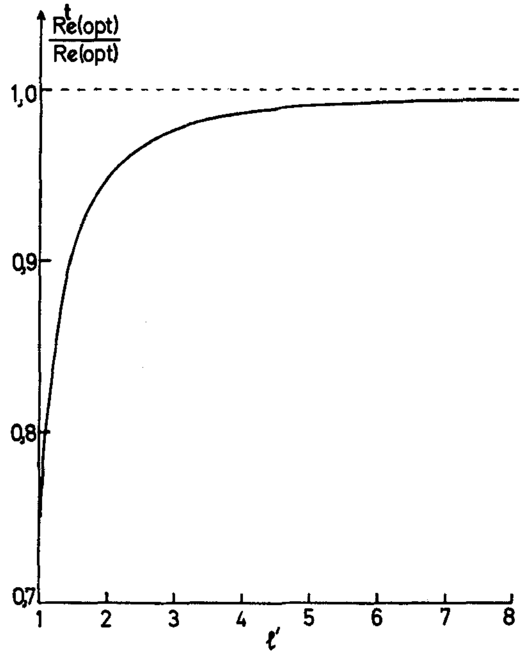


FIG. A1. Effect of B-term in plate height equation on optimum Re ($l' = l/l_a$).

APPENDIX 2

Functional Dependence of θ(opt)

Consider the Case B: E_p at Re(opt) is given by (see Table 2)

$$E_p = 2C_iFl(\alpha - 1)^2/3^{3/2}G_0C$$
$$= \frac{2C_iFl(\alpha - 1)^2k^2}{3^{3/2}16R^2(1 + k)^2(C_m + C_s)}$$
$$= YF(\theta)$$

where

$$Y = \frac{2C_iFl(\alpha - 1)^2}{3^{3/2}16R^2}$$

is independent of θ and the θ-dependence is included in

$$F(\theta) = \frac{k^2}{(1 + k)^2(C_m + C_s)}$$

The optimum in θ can in principle be solved from

$$\partial E_p/\partial\theta = 0$$

i.e., from

$$Y\frac{\partial F(\theta)}{\partial\theta} = 0$$

or

$$\frac{\partial F(\theta)}{\partial\theta} = 0 \qquad Y \neq 0$$

The only remaining variables in this equation are K, Scm, Scs, v_m, v_s, and θ, which shows that

$$\theta(\text{opt}) = \theta(K, \text{Scm}, \text{Scs}, v_m, v_s)$$

A similar result is obtained for Cases A and C (see Table 1).

SYMBOLS

B	parameter in plate height equation (Eq. 5)
C	parameter in plate height equation (Eq. 5)
C_i	concentration at the inlet
C_m	mobile phase contribution to C (Eq. 8)
C_s	stationary phase contribution to C (Eq. 8)
D_m	molecular diffusion coefficient in mobile phase
D_s	molecular diffusion coefficient in stationary phase
d_f	thickness of stationary phase liquid layer
E_p	chromatographic production rate
F	convenient parameter (Eq. 2)
G_1	convenient parameter (Eq. 2)
G_0	$= (\alpha - 1)^2 G_1$
H	plate height
K	concentration distribution coefficient
k	mass distribution coefficient
l	column length
l_a	minimum column length for start of production (zero yield at $H_{\min}$)
l'	$= l/l_a$
P_0	pressure at column outlet
R	resolution
Re	$= 2r_c u/v_m$: Reynolds number

Re'(opt)	optimum Re without neglect of B (Eq. A6)
Re(opt)	optimum Re with neglect of B (Eq. A7)
r_c	column radius
Scm	$= v_m/D_m$: Schmidt number for mobile phase
Scs	$= v_s/D_s$: Schmidt number for stationary phase
u	carrier gas flow velocity
V_i	sample inlet volume as measured at inlet pressure

Greek Letters

α	relative volatility
μ_m	viscosity of mobile phase
v_m	kinematic viscosity of mobile phase
v_s	kinematic viscosity of stationary phase
θ	$= d_f/r_c$

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Received by editor September 23, 1974