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Comparison of Parametric Pumping with Conventional Adsorption

A continuous thermal parametric pumping system is compared to a conventional adsorption system with thermal regeneration. Well-defined mathematical models are used to find the operating conditions which maximize the separation and throughput of each system.

Under practical operating conditions, the model equations indicate parametric pumping can process a larger volume feed stream at equivalent separations than conventional adsorption for the solute/adsorbent system studied. At equilibrium conditions equivalent results are obtained but parametric pumping requires more energy.

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SCOPE

Parametric pumping is a periodic separation technique which represents an alternative to conventional adsorption processes. This concept requires a solute/adsorbent system in which some controllable thermodynamic variable affects the solute equilibrium distribution between the fluid and solid phases. Significant separations were reported using a periodic temperature change coupled with a periodic flow in a packed bed of adsorbent (Wilhelm et al., 1968). A quantitative comparison of a parametric pumping process and a conventional adsorption process for a specific solute/adsorbent equilibria is presented here.

Model equations for the two processes are used which assume realistic, finite mass transfer between the fluid and solid phases. The optimum operating conditions for the two processes are determined using a numerical solution of the model equations. The maximum separations and throughputs for each process are compared under the assumption that the physical equipment is the same in both cases.

CONCLUSIONS AND SIGNIFICANCE

The parametric pumping process investigated can process a larger volume feed stream at equivalent separations than the conventional adsorption process for practical operating conditions. The comparison between the parametric pumping process and conventional adsorption is shown in Figure 9. A dimensionless feed rate is plotted versus the solute remaining in the product. This plot is then the separation/throughput plane for comparison. The desired operating conditions are those which yield the lowest remaining solute and the highest throughput. The curves represent the optimum conditions with the region to the right and below each curve as the accessible space for each process. At the limiting condition of zero feed rate equilibrium is achieved and the conventional process gives the best possible separation for the given solute/adsorption system. The one-column parametric pumping system illustrated in Figure 2 gives better results for all nonequilibrium conditions and equivalent results at equilibrium to the conventional process.

These results indicate that parametric pumping represents an alternate adsorption processing technique with improved results over a conventional process. Because of the more frequent changes in temperature in the optimum parametric pumping process, the energy requirements will, in general, be higher than those of conventional adsorption.

Adsorption is the most feasible solution presently known for many tertiary treatment separations. We are interested in improving the efficiency of these separations. In addition, an improved process would expand the use of adsorption into areas where it is now only marginally acceptable. In taking this approach, it is recognized that adsorption is not necessarily the best solution for all tertiary treatments, but that each separation problem must be considered individually.

A qualitative discussion of the differences between cyclic processes such as parametric pumping and conventional adsorption processes was given by Harris (1970). Horn and Lin, (1969) compared steady state adsorption and extraction processes with parametric pumping and showed equivalent results for an equilibrium system with linear isotherms. The steady state processes required the transport of the solid phase while the cyclic process had a heat recovery problem. A quantitative comparison of conventional adsorption with parametric pumping is made in this paper for a nonequilibrium system with nonlinear isotherms.

Conventional adsorption processes suffer from several disadvantages which have limited their application and impose a limit to their efficiency, such as relatively high capital investment to supply required capacity, regeneration stream concentration too low for direct recycle to the main process, and secondary pollution effects. The goal of a modified adsorption process is to overcome some of the disadvantages of conventional operation. Periodic adsorption systems such as parametric pumping appear to alleviate many of these problems, although introducing other disadvantages such as lower energy efficiency. In general, these systems are self-regenerating as discussed below. Thus, the system is always on stream and multiple columns are not required for continuous operation as with the conventional method. This offers the possibility of increasing the separating capacity for a given column using periodic operations. This is the major point investigated in this work.

Parametric pumping in a packed column couples a cyclic reverse in flow direction with a change in a thermodynamic variable, such as temperature. The change in temperature affects the solute equilibrium distribution between fluid and solid phases in the adsorption column. The major difference from conventional adsorption is that the column is not completely saturated and then regenerated on alternate cycles. The technique has been demonstrated experimentally to yield large separations in batch systems (Wilhelm et al., 1968).

A comparison is made between conventional adsorption and a recuperative parametric pumping process where heat is introduced to a packed column of adsorbent from the ends. The recuperative mode is of more practical interest than the direct mode of parametric pumping where heat is introduced through the walls of the column leading to significant heat transfer problems.

The constraints on this comparison are illustrated schematically in Figure 1. A black box separation unit is shown with the necessary input and output streams. The separation unit will be either a conventional adsorption process or some type of parametric pump. The regeneration stream with flow rate Q_R is required only for the conventional process. For a given adsorbent/solute system, the optimum separation of the different processes are found for arbitrary adsorbent column size and feed rate Q_F. The separating efficiency is defined in terms of the solute remaining in the purified stream compared to the solute in the feed stream, that is,

$$\frac{C_B Q_B}{C_F Q_F}$$

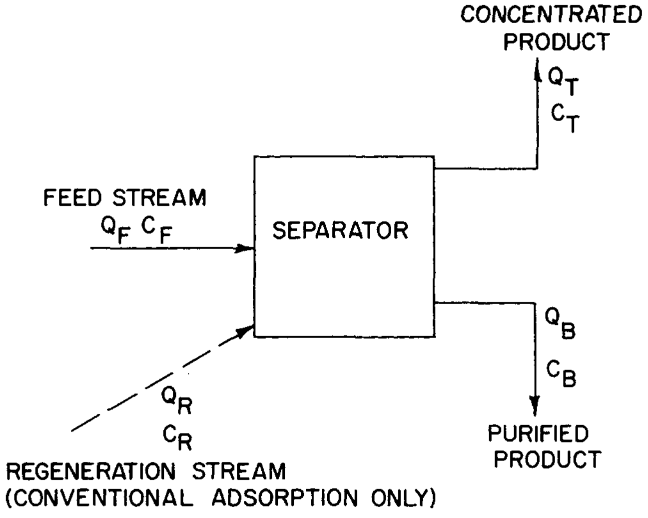

Fig. 1. Schematic of separation problem.

The total amount of concentrated product Q_T is assumed to be fixed with respect to the feed rate at a value of $Q_F/Q_T = 3$. The flow rate of the purified product Q_B is greater for a given feed rate with conventional adsorption because of the addition of the regeneration stream and the assumed constraint made above on Q_T.

Model equations for the two processes are used which assume realistic, finite mass transfer between the fluid and solid phases. That is, the residence time of the adsorption system effects the local approach to equilibrium and therefore the ultimate separation possible. The separation/capacity space is mapped for the processes to indicate the relative merits of each system considered.

PARAMETRIC PUMPING SYSTEMS

The basic separation mechanism of parametric pumping has been discussed previously (Wilhelm et al., 1968; Wilhelm and Sweed, 1968). Detailed models and experimental data have been given for both the recuperative mode (Wilhelm et al., 1968) and the direct mode (Chen and Hill, 1971; Wilhelm et al., 1968) of parametric pumping for both batch and continuous systems.

The advantage of the recuperative mode is that it avoids the difficult heat transfer problem of the direct mode for large-scale systems. However, for fluid displacements less than one column volume per half cycle, the entire column never experiences the maximum change in temperature, hence the differences in the solute equilibrium at any given point in the system would not be as great in the recuperative mode. Thus, the separation obtained by the recuperative mode is never as large as that obtained for the direct mode. However, for many real systems this effect can be minimized if the slope of the equilibrium isotherm is large. This is the case when the capacity of the packing to adsorb solute is large. In this case the optimum fluid displacement for a half cycle is many column volumes. For many real systems the thermal wave travels through the column faster than the mass wave. This allows the direct mode behavior to be approached by heating and cooling only at the ends of the column. The recuperative mode of parametric pumping will be considered exclusively in this work.

Two continuous parametric pumping systems will be considered in detail. The number of possible process arrangements is large and the ones chosen are meant to be representative. The first requires only one column and has both product streams and the feed stream flowing at all times. The second system requires two columns with the feed stream entering the system at a continuous rate but only one product stream exiting the system at any time.

The first system shown in Figure 2 is adapted from an arrangement proposed by Chen and Hill (1971). The feed rate, top product rate, and bottom product rate are held constant and equal to $(X_T + X_B)Q_F$, X_TQ_F, and X_BQ_F, respectively. During the first half of a cycle, fluid flows up the column from the bottom reservoir. Part of this stream is diverted to the bottom product. The feed stream is combined with the top effluent and then split into two streams. Part goes to the top product and the remainder to the top reservoir. On the second half of the cycle fluid from the top reservoir is split with part going to the top product. The remainder is combined with the feed stream and goes to the column. The effluent from the bottom of the column is split between the bottom product and the bottom reservoir. The reflux ratio of this system is determined by the split of the stream at the top of the column between the top reservoir and the top product. The product concentrations of interest are the averages over one cycle.

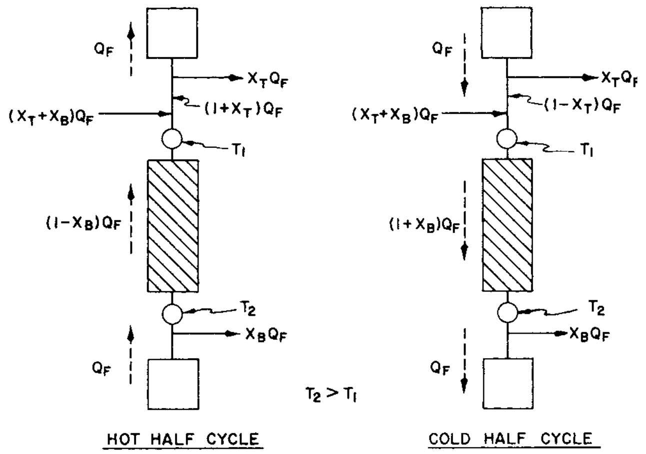

Fig. 2. Continuous one column parametric pumping system.

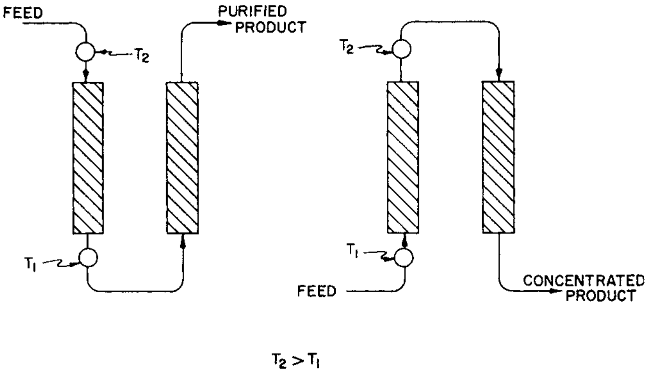

Fig. 3. Continuous two column parametric pumping system.

The second system, shown in Figure 3, requires two columns. In this system the first column is fed at the top during the first portion of the cycle and fed at the bottom during the second portion of the cycle. In general, the duration of the two portions of the cycle are not equal, but the feed rate Q_F is held constant. The ratio of top to bottom product volume is varied by changing the ratio of the times for the two portions of the cycle.

CONVENTIONAL ADSORPTION SYSTEM

The conventional adsorption system used as a basis of comparison with the parametric pumping operations is discussed in this section. A thermal regeneration system is assumed to allow a direct comparison with thermal parametric pumping. The difference between the conventional adsorption system considered here and parametric pumping is then only in the method of operation. This is manifested in the timing of the alternating cycles in each system. Conventional adsorption flows in a single direction until column capacity is reached and the column is then regenerated. Parametric pumping allows the variation of the relative cycle times and, in general, the column will never be saturated or fully regenerated. Thus, conventional adsorption with thermal regeneration can be considered as a limiting case at one end of the possible operating range of parametric pumping.

The specific conventional system considered here is shown in Figure 4. A feed stream is added continuously

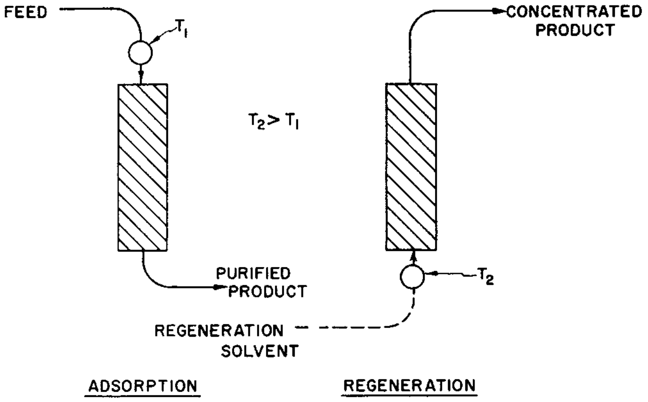

Fig. 4. Conventional adsorption with thermal regeneration.

to the column at a constant concentration and temperature during the adsorption cycle. During regeneration, pure solvent (for example, water) is added at an elevated temperature. In order to make a comparison with parametric pumping, the ratio of the total volume of the concentrated product stream to the feed stream is held constant at 1:3 as indicated previously.

MODEL EQUATIONS AND DIMENSIONLESS PARAMETERS

The equations which describe adsorption in a packed bed in general include material balances for $n - 1$ components, an energy balance, and an expression describing the equilibrium distribution of material between the liquid and solid phases. The model developed here is for a binary system which requires only one material balance. Axial dispersion is assumed negligible for both the mass and energy balances. In addition, plug flow is assumed in the packed bed and mass transfer effects are assumed to be lumped in a film around the solid particle.

Using the following dimensionless variables:

$$\phi_f = \frac{C_f}{C_0}, \quad \phi_s = \frac{C_s}{C_0}\frac{\rho_s}{\epsilon}, \quad \phi_f^* = \frac{C_f^*}{C_0},$$

$$\theta_f = \frac{T - T_0}{\Delta T_0}, \quad \theta_s = \frac{T_s - T_0}{\Delta T_0},$$

$Z = Z'/L$ and $t = t'/\tau$, where L is the length of the column and τ is a residence time, a differential mass balance on the solute can be written as

$$\alpha f(t)\frac{\partial \phi_f}{\partial Z} + \frac{\partial \phi_f}{\partial t} + \frac{\partial \phi_s}{\partial t} = 0 \tag{1}$$

where ϕ_f and ϕ_s are the solute concentrations in the liquid and solid phases, respectively.

Interphase mass transfer between solid and liquid is assumed to be of the following form:

$$\frac{\partial \phi_s}{\partial t} = \lambda(\phi_f - \phi_f^*) \tag{2}$$

where ϕ_f^* is the liquid phase concentration that would be in equilibrium with the solid phase concentration.

A differential energy balance is given by

$$\alpha f(t)\frac{\partial \theta_f}{\partial Z} + \frac{\partial \theta_f}{\partial t} + \beta\frac{\partial \theta_s}{\partial t} = 0 \tag{3}$$

and the interphase heat transfer expression is

$$\frac{\partial \theta_s}{\partial t} = \gamma(\theta_f - \theta_s) \tag{4}$$

The energy and mass balances are coupled by the equilibrium distribution expression

$$\phi_f^* = \phi_f^*(\theta_s, \phi_s) \tag{5}$$

Thus, the equilibrium fluid concentration is a function of the solid concentration and the local temperature.

The equilibrium distribution function used in this work is given as a Freundlich isotherm

$$C_s = a(C_f^*)^b \tag{6}$$

where the temperature dependence is lumped in the preexponential factor.

$$a = a_0 e^{\frac{E}{RT}} \tag{7}$$

The dimensionless form is then

$$\phi_s = \frac{\rho_s}{\epsilon} a C_0^{b-1} (\phi_f^*)^b \tag{8}$$

The dimensionless parameters are defined as dimensionless fluid displacement per cycle

$$\alpha f(t) = \frac{v(t)\tau}{L} \tag{9}$$

dimensionless mass transfer coefficient

$$\lambda = \frac{k_m \tau}{dp} \tag{10}$$

dimensionless heat transfer coefficient

$$\gamma = \frac{h_1 \tau}{(\rho C_p)_s d_p} \tag{11}$$

ratio of heat capacities of the solid and liquid phases

$$\beta = \frac{(C_p)_s}{(C_p)_f} \tag{12}$$

EFFECT OF FLUID VELOCITY AND TEMPERATURE ON γ AND λ

The dimensionless heat transfer coefficient γ is obtained below in terms of the dimensionless mass transfer coefficient λ. The temperature and velocity dependence of λ is then shown. These relations combined with the differential heat and mass balances, heat and mass transfer expressions, and the equilibrium function constitute the model equations for the adsorption systems of interest. The method of solution of the model equations is the "STOP-GO" method used by Sweed and Gregory (1971).

The ratio of the dimensionless heat and mass transfer coefficients is

$$\frac{\gamma}{\lambda} = \frac{h_1}{(\rho C_p)_s k_m} \tag{13}$$

We assume j-factor correlations for k_m and h_1 (Bird et al., 1960)

$$j_D = \frac{k_m}{v}(Sc)_f^{2/3} \tag{14}$$

where $Sc = \left(\frac{\mu}{\rho D}\right)_f$

and

$$j_H = \frac{h_1}{C_p \rho v_0}\left(\frac{C_p \mu}{k}\right)_f^{2/3} \tag{15}$$

If we assume $j_H = j_D$ (Bird et al., 1960), then using Equations (11) and (12),

$$\frac{h_1}{k_m} = \left(\frac{k}{\rho D C_p}\right)_f^{2/3} \frac{(C_p\rho)_f v_0}{v} \tag{16}$$

but

$$v_0 = v\epsilon$$

$$\frac{h_1}{k_m} = \left(\frac{k}{\rho D C_p}\right)_f^{2/3} (C_p\rho)_{f\epsilon} \tag{17}$$

Substituting into Equation (13),

$$\frac{\gamma}{\lambda} = \left(\frac{k}{\rho D C_p}\right)_f^{2/3} \frac{(C_p\rho)_{f\epsilon}}{(C_p\rho)_s} \tag{18}$$

The dimensionless heat transfer coefficient γ changes very slightly with temperature in the range of interest. Since the fluid velocity does not appear in Equation (18), the dependence of this ratio on temperature and velocity is the same as the dependence of λ.

In general, the interphase mass transfer coefficient will be a function of the fluid velocity. For most adsorbent systems of interest, the controlling mass transfer resistance can be considered as lumped in a film around the solid particle.

As shown by Sweed and Gregory (1971), if the desired mass transfer coefficient λ is compared to a base case λ_0 for the same system at constant temperature, then

$$\lambda = \lambda_0 \left[\frac{v}{v_0}\right]^{1-a} \left[\frac{\tau}{\tau_0}\right] \tag{19}$$

The value of the exponent a for this work is taken from the literature (Sweed and Gregory, 1971) as $a = 0.7$. Thus, the relative velocity dependence of the interphase mass transfer coefficient is given by

$$\lambda = \lambda_0 \left[\frac{v}{v_0}\right]^{0.3} \left[\frac{\tau}{\tau_0}\right] \tag{20}$$

The temperature effect on the dimensionless mass transfer coefficient is fitted from data in the literature (Sweed and Gregory, 1971) and assumed to be representative of aqueous systems. Using an exponential form,

$$\frac{\lambda}{\lambda_0} = e^{-\frac{E_M}{R}\left(\frac{T - T_0}{T T_0}\right)} \tag{21}$$

Thus, once a room temperature dimensionless mass transfer coefficient λ_0 is selected, the ratio γ/λ and Equations (20) and (21) are used to determine γ and λ for all temperatures and fluid velocities.

In order to put all comparisons on an equivalent basis, they must be related to some base system with an arbitrary feed rate and residence time. To do this, an arbitrary fixed column size is used. The dimensionless mass transfer coefficient λ is a function of the actual local mass transfer coefficient k_m and the fluid velocity in the column itself. The actual mass transfer coefficient depends on the specific system considered. To provide a general comparison, k_m is not specified but instead the effect on each system of the dimensionless mass transfer coefficient is investigated over a wide range. The fluid velocity in the column is related to the feed rate, the overall residence time, and the reflux ratio.

The desired comparison requires a fixed feed rate to a column of fixed size. This feed rate can be expressed in dimensionless form as proportional to the overall dimensionless mass transfer coefficient. These conditions are specified by choosing an arbitrary residence time τ_0 such that

$$\tau_0 = \frac{V_c}{Q_F} \tag{22}$$

where V_c = column volume and Q_F = flow rate of the feed stream. Then, from the definition of λ,

$$\frac{1}{\lambda_B} = \frac{d_p}{k_m} \frac{Q_F}{V_c} \tag{23}$$

where d_p = the particle size of the solid adsorbent in the column. The reciprocal of the dimensionless mass transfer coefficient $1/\lambda_B$ is effectively a dimensionless feed rate for a given system. The parameter λ_B is then taken as the base case. However, the actual λ to be used in the calculations within the column will, in general, be altered depending on reflux and the way the column is operated. The base residence time is given by the total volume of feed stream per unit column volume in a given time period. For example, during the normal cycle for conventional adsorption, part of the input to the system is regeneration solvent. Thus, the total volume of fluid actually introduced to the column is increased. This has the effect of lowering the actual λ within the column. This effect is taken into account using Equation (20).

The values used for the constants at room temperature in the model equation are given in Table 1.

Table 1. Values for Constants at Room Temperature

C_{Pf} = 1.0 cal/g °K
k_f = 1.45×10^{-3} cal/s cm °K
ρ_s = 1.7×10^3 g/l
C_{ps} = 0.25 cal/g °K
D = 1.0×10^{-5} cm^2/s
ρ_f = 1.0 g/cm^3
C_0 = 1×10^{-4} g-mole/l
E_M = 4.7 kcal/g-mole
a_0 = 1.32×10^{-4}
b = 0.181
E_a = 4.0 kcal/g-mole

All of the parameters except a_0 are representative of phenol adsorption from water on activated carbon (Fox et al., 1970). The equilibrium was altered to create a solid adsorbent with a much lower capacity for phenol than normally encountered with activated carbon. This greatly reduces the computer time required to numerically solve the model equations and allows a much more detailed scan of operating parameters.

The effect of the equilibrium function on the generality of the results for the comparisons made here has not yet been completely defined. The temperature dependence of the isotherms is also not well known for the phenol/water/carbon system. The relation used here is only approximate.

COMPARISON RESULTS

In this section, the results of the comparison between conventional adsorption and parametric pumping are given. First the optimum conditions for the conventional system are presented under the constraints described in previous sections. Results for two parametric pumping systems are then summarized. Finally, an overall comparison is made.

The overall residence time has been fixed in all of these systems. This is the residence time defined by the feed rate and size of the column. In general, all of the process systems have an optimum cycle time. That is, for a given feed rate the length of the cycle may be varied.

In Figure 5, the parameter λ_B is plotted versus the separation for the conventional adsorption system. The parameter λ_B is effectively the reciprocal of the dimensionless feed rate as shown above. The separation parameter of interest is the total solute remaining in the purified product stream compared with the total solute fed to the system. The parameter α shown in Figure 5 is the dimensionless displacement of fluid within the column in terms of column volumes of fluid per cycle. As shown, the separation becomes poorer with increased throughput, that is, decreased λ_B. Some representative curves are shown in Figure 5 which define an envelope in the separation-capacity plane. Thus the region of small λ_B (high throughput) and low remaining solute (excellent separation) is not accessible by conventional adsorption. From Figure 5 a value of $\alpha = 4.4$ is found to give the optimum separation for this system under the constraints assumed.

The first parametric pumping unit considered uses a single column as shown in Figure 2. Optimum conditions with respect to displacement per cycle also exist for this system. This unit allows the reflux ratio to be varied. The reflux ratio reflects the fraction of fluid leaving the column on a half cycle which is returned to the column on the succeeding half cycle.

The optimum operating conditions for the single column parametric pumping arrangement are defined by the results given in Figures 6 and 7. Figure 6 shows separation versus α for several values of λ_B at a reflux ratio of $R = 5.0$. Separation improves with increasing reflux ratio although the change is small above $R = 5.0$. The energy consumption for this system increases with increasing reflux ratio since the temperature of the column is changed more often. An optimum dimensionless displacement α also exists for this system.

Some results for the two-column system shown in Figure 3 are presented in Figure 8. Separation is plotted versus dimensionless displacement α for several values of λ_B. Again an optimum α exists although the value changes slightly with changes in λ_B. Figure 8 gives the optimum operating conditions for this system.

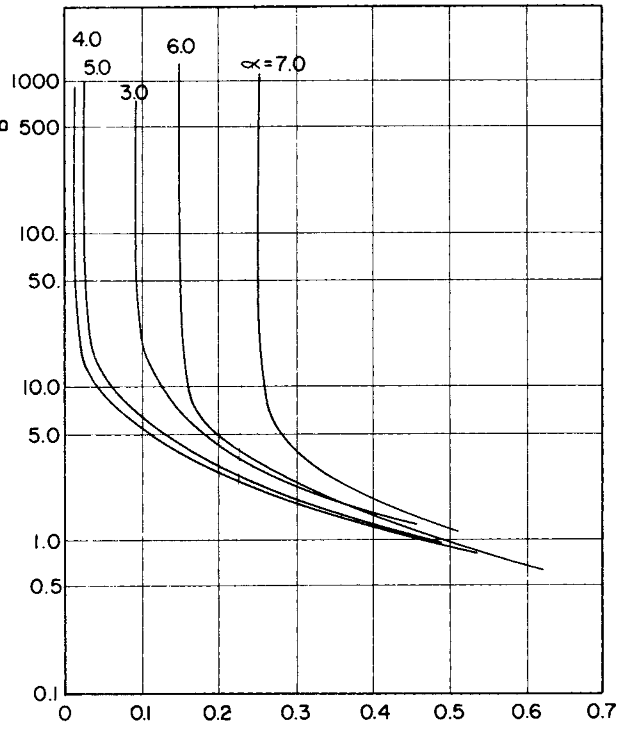

Fig. 5. The capacity/separation plane for conventional adsorption.

The final overall comparison of the three systems con-

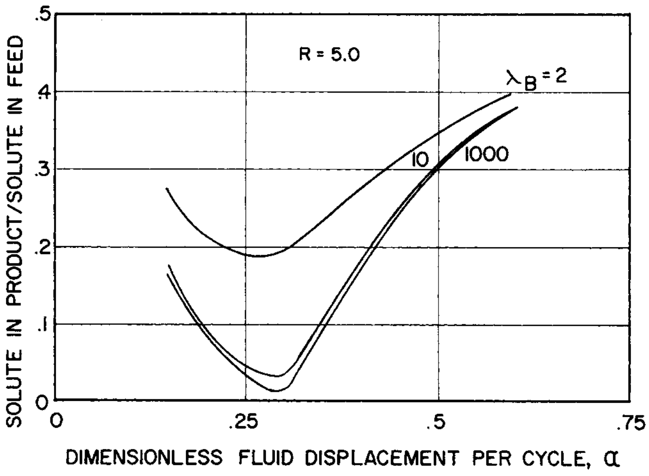

Fig. 6. The effect of displacement on separation for a one column parametric pumping system with λ_B as a parameter.

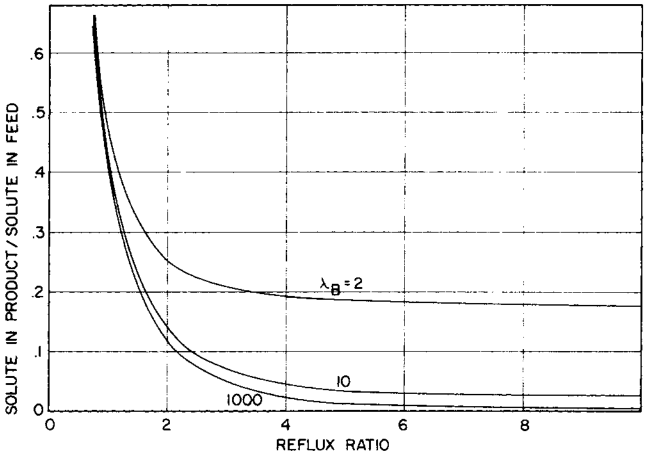

Fig. 7. The effect of reflux ratio on separation for a one column parametric pumping system with λ_B as a parameter.

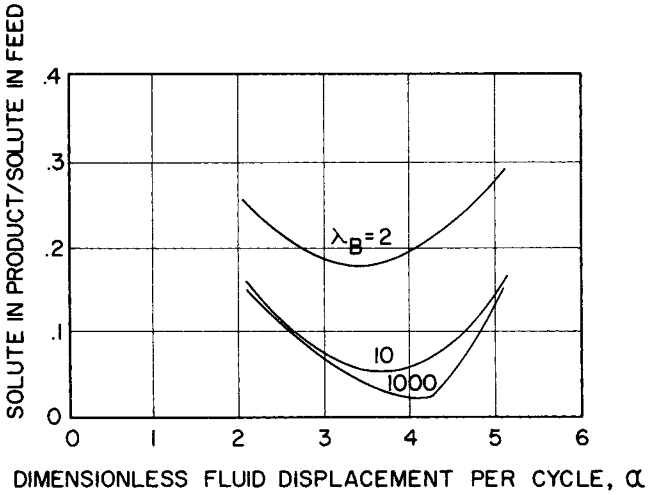

Fig. 8. The effect of displacement on separation for a two column parametric pumping system with λ_B as a parameter.

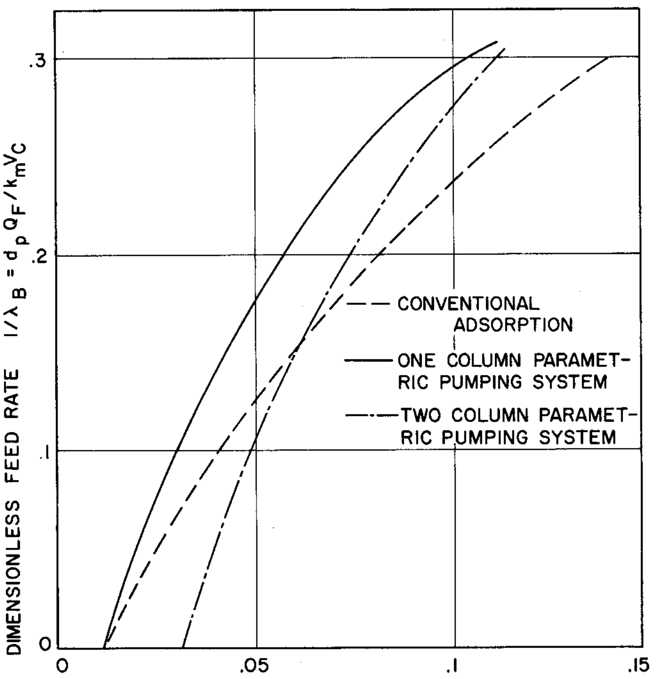

Fig. 9. Overall comparison of conventional adsorption and parametric pumping-dimensionless feed rate vs. separation.

sidered is shown in Figure 9. The dimensionless feed rate $d_p Q_F / k_m V_c$ is plotted versus separation. As the feed rate approaches zero, all the systems approach equilibrium operation. The two-column system is compared on the same capacity basis as the other units. The optimum two-column conventional adsorption system operates with the two columns in parallel. Thus the separation characteristics are the same as the one-column system at double the capacity.

At equilibrium the conventional adsorption unit and the one-column parametric pump give the same separation which, in turn, is better than the two-column unit investigated. As the throughput is increased, the separating capability of the conventional unit falls off more rapidly than either of the parametric pumping systems. Thus at any nonzero feed rate the one column parametric pump is superior to conventional adsorption. At some finite capacity the two-column parametric pumping unit also becomes superior to the conventional system.

These results show for a given system that parametric pumping systems exist which can process a larger volume feed stream at equivalent separations compared with conventional adsorption. There are, of course, many other variations of parametric pumping systems using both single and multiple columns which may give results superior to those shown here.

The improved separation of parametric pumping at finite feed rates can partially be explained in terms of increased contact time between the solid and liquid phases at a given position in the column. During any time period, more fluid must flow through the column in the conventional process than with parametric pumping because of the required regeneration of the column. The additional flow of regeneration solution reduces the local contact time between solid and liquid in the conventional system. This reduction in contact time is reflected in a reduction in the amount of mass transferred per cycle, hence less efficient separation. At equilibrium conditions obtained in the limit of zero flow rate, conventional adsorption and parametric pumping yield the same separation. However, equilibrium conditions are not realized in practical applications.

NOTATION

C_f = fluid phase concentration, g-mole/l
C_f^* = equilibrium fluid phase concentration, g-mole/l
C_s = solid phase concentration, g-mole/g adsorbent
C_0 = reference fluid concentration, g-mole/l
C_p = heat capacity, cal/g °K
d_p = adsorbent particle diameter, cm
E = activation energy, cal/g-mole
h_1 = heat transfer coefficient, cal/s-cm^2-°K
k_f = thermal conductivity, cal/s-cm-°K
k_m = mass transfer coefficient, cm/s
L = length of column, cm
Q_F = feed rate, cm^3/s
T = temperature, °K
t' = time, s
t = time, dimensionless
v = fluid velocity, cm/s
V_C = column void volume, cm^3
X = product flow rate/reservoir displacement flow rate
Z' = axial column position, cm
Z = dimensionless axial column position
α = dimensionless displacement of fluid per cycle
β = heat capacity ratio
γ = dimensionless overall heat transfer coefficient
ϵ = column void fraction, ml void/ml column
θ_f = dimensionless fluid temperature
θ_s = dimensionless solid temperature
λ = dimensionless overall mass transfer coefficient
ρ_s = adsorbent density, g/l adsorbent
τ = residence time, s
ϕ_f = dimensionless fluid concentration
ϕ_f^* = dimensionless equilibrium fluid concentration
ϕ_s = dimensionless adsorbent concentration
μ = fluid viscosity, cps

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