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Nonisothermal Adsorption: Separation of Gas Mixtures by Modulation of Feed Temperature

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Abstract

The purpose of this article was to present the principles and experimental examples of an adsorption process for separating gas mixtures characterized by the following features: the mixture to be treated contains a major component and a minor component, it is desired to produce a fraction of the pure major component and a fraction enriched in the minor component, the adsorbent and the operating conditions are chosen in such way that the major component is essentially not adsorbed, no carrier or purge gas is used, and the regeneration of the adsorbent is obtained with the gas mixture feed heated at a suitable temperature. The experimental example given deals with a mixture of *n*-pentane/isopentane on a Linde 5A molecular sieve. The process is based on the coupling between temperature and adsorption, as are other temperature swing processes such as cycling zone adsorption. A proper choice of parameters of the temperature modulation (low and high temperature, durations of cold and hot step) leads to a "resonance" where the concentration variation is maximal and a fraction of the pure major component can be obtained. It is shown how these parameters are determined from a knowledge of the adsorption isotherms and from simple experiments. The influence of factors such as total pressure and specific heat of the gases is discussed.

INTRODUCTION

Adsorption is usually an exothermal process. Heats of adsorption commonly reach values as high as 10 kcal/mole. When adsorption occurs in the dynamic regime in a narrow column (such as a chromatographic

column), the heat evolved is rapidly removed through the walls, and the adsorbent bed remains practically isothermal. This is no longer true in an industrial column of large diameter. As adsorbents are often poor conductors, the heat evolved increases the temperature of the adsorbent or is carried away by the convective flow.

Nonisothermal adsorption has been treated with a variety of approaches depending on the authors. Leavitt (*1*) was the first to show experimentally the existence of two distinct transfer zones during the nonisothermal adsorption of a gas in a column packed with adsorbent. Several authors have used sophisticated models, including mass and heat transfer resistances and axial dispersion, the solution of which requires case by case computer calculations. Although such models are necessary when a quantitative fit of experimental results is required, they generally bring little insight to the fundamental processes which are blurred by second-order effects.

THE EQUILIBRIUM MODEL

A more fundamental approach has been taken by authors who use the so-called "equilibrium theory" (*2–5*). This model, assuming *local* thermodynamic equilibrium and thus neglecting hydrodynamic dispersion and transfer resistances, has the advantage of putting forward the fundamental first-order effects: curvature of adsorption isotherm, heat of adsorption, etc.

The equilibrium theory leads to a set of partial differential equations (PDE) which express differential mass and enthalpy balances. For example, in the case of adiabatic, isobaric adsorption, we write

$$\frac{\partial}{\partial z}(\phi_c{}^i) + \varepsilon\frac{\partial}{\partial t}(C^i) + (1-\varepsilon)\frac{\partial}{\partial t}(C_s{}^i) = 0, \qquad i = 1,\ldots,n \tag{1}$$

$$\frac{\partial}{\partial z}(\Phi_h) + \varepsilon\frac{\partial}{\partial t}(h) + (1-\varepsilon)\frac{\partial}{\partial t}(h_s) = 0 \tag{2}$$

where ε is the porosity of the packing (nondimensional)
$\phi_c{}^i$ is the flux of component i through a straight cross-section of the column of unit area (mole sec^{-1} cm^{-2})
Φ_h is the corresponding enthalpy flux (cal sec^{-1} cm^{-2})
C^i is the concentration of component i in the fluid (mole cm^{-3})
$C_s{}^i$ is the quantity of component i adsorbed per unit volume (mole cm^{-3})
h is the enthalpy of the fluid per unit volume (cal cm^{-3})
h_s is the enthalpy of the solid unit per volume (cal cm^{-3})

z and t are distance and time, respectively (cm, sec)

In vectorial notation, letting

$$\mathbf{\Phi} = \begin{vmatrix} \phi_c{}^1 \\ \vdots \\ \phi_c{}^n \\ \phi_h \end{vmatrix} \qquad \frac{\mathbf{C}}{\varepsilon} = \begin{vmatrix} C^1 \\ \vdots \\ C^n \\ h \end{vmatrix} \qquad \frac{\mathbf{C}_s}{1-\varepsilon} = \begin{vmatrix} C_s{}^1 \\ \vdots \\ C_s{}^n \\ h_s \end{vmatrix} \tag{3}$$

the system of Eqs. (1) and (2) is rewritten

$$\frac{\partial}{\partial z}(\mathbf{\Phi}) + \frac{\partial}{\partial t}\mathbf{C} + \frac{\partial}{\partial t}\mathbf{C}_s = 0 \tag{4}$$

The equilibrium theory assumes an algebraic relation

$$\mathbf{C}_s = \mathbf{C}_s(\mathbf{C}) \tag{5}$$

relating for each component the amount adsorbed to the concentration in the fluid phase. An example of such a relation is the generalized Langmuir isotherm:

$$C_s{}^i = \frac{C_M K^i C^i}{1 + \sum_{i=1}^{n} K^i C^i} \tag{6}$$

In addition, we assume a relation between the isotherm coefficients (the K^i in Langmuir's equation), absolute temperature T, and the heat of adsorption ΔH^i, which may be of the Arrhenius type:

$$K^i = K_0{}^i \sqrt{T} \exp\left(-\Delta H^i / RT\right) \tag{7}$$

Temperature and concentration are thus coupled through Eqs. (6) and (7), and also through the dependence of h_s on the C_s and temperature. Using the isotherm equations, $\mathbf{C}_s$ can be eliminated in Eq. (4). Moreover, the flux $\mathbf{\Phi}$ can be expressed as the product of the fluid velocity u and the fluid concentration vector $\mathbf{C}$. If u is constant, the system of equations then contains only the unknown $\mathbf{C}$.

SOLUTION BY THE METHOD OF CHARACTERISTICS

It can be shown (*6*) that such quasi-linear systems lead to an eigenvalue problem. If all eigenvalues are real and distinct, the system is said to be totally hyperbolic. When this is the case, the so-called "method of characteristics" applies, which reduces the PDE to an ODE (ordinary differential equation) along certain particular "characteristic directions." The details of the method of characteristics can be found in classical mathematical textbooks (*6*) and here we shall merely use its results.

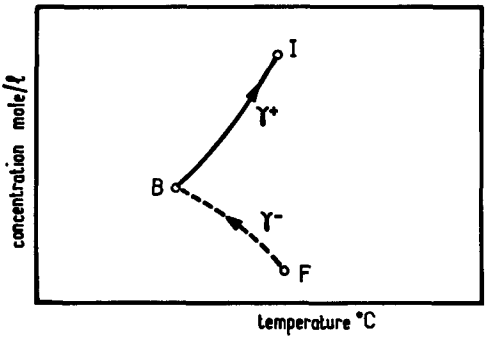

FIG. 1. Response to a step change in temperature and concentration; traject in the (C, T) plane.

In the case where there is only one adsorbable component in the gas, the method of characteristics leads to a convenient graphical representation of the solutions of the ODE in the concentration–temperature plane or (C, T) plane. This representation* has been used by Rhee and Amundson (*4*, *5*) in the case of constant fluid velocity u, and by Pan and Basmadjian in the case where the accumulation term in the gas $(\partial c/\partial t)$ is negligible compared to the accumulation in the solid $(\partial c_s/\partial t)$. This implies that the mass flow rate of nonadsorbed components may be assumed constant. We have shown (*8*) that the above hypotheses are unnecessarily restrictive, and that a similar representation of the solutions is found when the fluid velocity varies.

GRAPHICAL REPRESENTATION OF SOLUTIONS

We shall be concerned with the solutions corresponding to a step change in inlet conditions to the column. In the concentration–temperature plane, let us designate by $I\,(C_I, T_I)$ the point representing the initial condition of the column, assumed uniform. Let $F(C_F, T_F)$ be the point representing the new inlet conditions. In the (C, T) plane there exists a traject connecting F to I, and composed of two integral curves of the system of ODE derived from the original PDE by the method of characteristics.

Let γ^+ and γ^- be these two curves (Fig. 1). Each point on these curves represents a couple (concentration, temperature) which propagates as a whole in the column at its own velocity. γ^+ and γ^- each correspond to a "transfer zone" or wave of concentration and temperature which propagates through the column. Let Point B, the intersection of the two

*A similar representation is used in multicomponent chromatography where concentration plays the role of temperature here (see Ref. 7, for example).

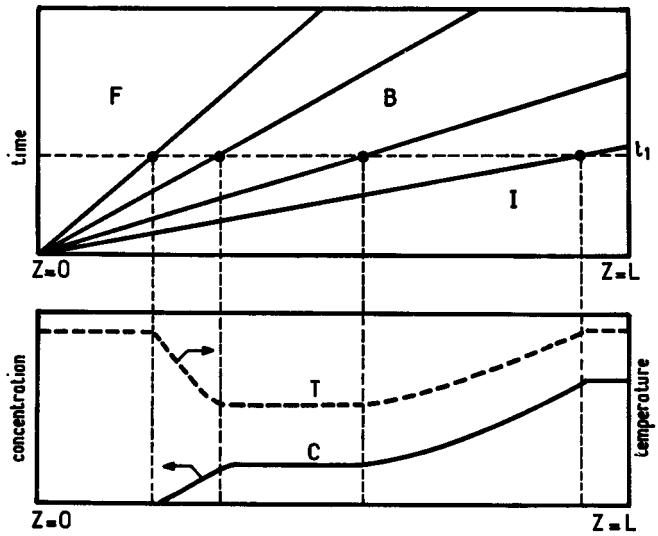

FIG. 2. Construction of a concentration and temperature profile in a column from a distance–time diagram, for a time $t = t_1$.

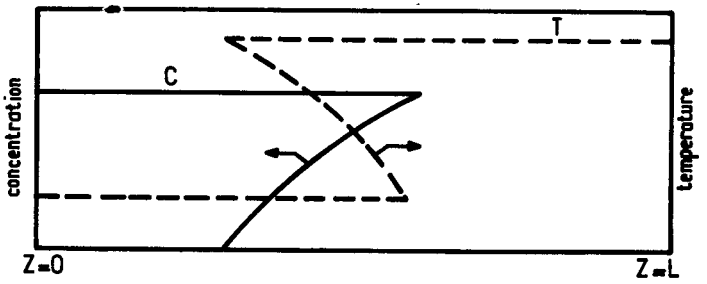

FIG. 3. Unrealistic (overhanging) profiles obtained from continuous solution when a shock wave occurs.

curves, correspond to one of two velocities, depending on whether it is considered as belonging to γ^+ or to γ^-. In the column, Point B corresponds to a zone of constant concentration and temperature, or a "plateau," separating the two transfer zones.

To each point on γ^+ or γ^- we can associate a curve in the (z, t) plane, the slope of which is the velocity of propagation of the corresponding couple of concentration and temperature. Fig. 2 shows how, from such a diagram, a profile in the column can be constructed at any given time t_1.

By this method, unrealistic overhanging profiles may sometimes be obtained, such as that shown on Fig. 3.

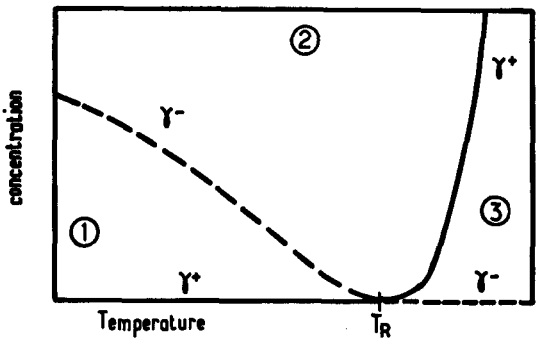

FIG. 4. The three zones in the (X, T) plane.

This solution expresses the existence of a "shock wave" which is a discontinuous solution of the physical problem for which the differential Eqs. (1) are no longer valid and must be replaced by a set of finite difference equations (FDE). Calling ΔA the change in an entity A across the shock moving at a velocity v, the differential system 1 is then replaced by the system of FDE:

$$\Delta\phi^i = v[\Delta C^i + \Delta C_s^i], \qquad i = 1,\ldots, n$$
$$\Delta\phi_h = v[\Delta h + \Delta h_s] \tag{8}$$

In a fashion similar to the continuous case, after eliminating v, these equations allow the construction, through any point (C_0, T_0) of the (C, T) plane, of two curves Σ^+ and Σ^-. These curves represent the loci of the (C, T) couples which can possibly form a shock with (C_0, T_0). In the following we shall ignore the distinction between γ's and Σ's. We shall use only γ's, keeping in mind that in certain cases they have to be replaced by Σ's.

GENERAL PROPERTIES OF THE (C, T) OR (X, T) PLANE

We restrict ourselves to a single adsorbable component and use, instead of a molar concentration C, the mole percentage X of adsorbable component in the mixture $(0 < X < 100)$. The (X, T) plane is divided into three zones by two particular γ's, both tangent to the axis $X = 0$ for a temperature T_R, which we call the "reversal temperature" (Fig. 4). T_R is the temperature at which the slope of the adsorption isotherm (at $X = 0$) equals the ratio of the specific heats of the column packing (including walls) to the specific heat of the nonadsorbable gas.

Expressed more intuitively (but less rigorously), T_R is the temperature below which heat propagates faster in the column than concentration

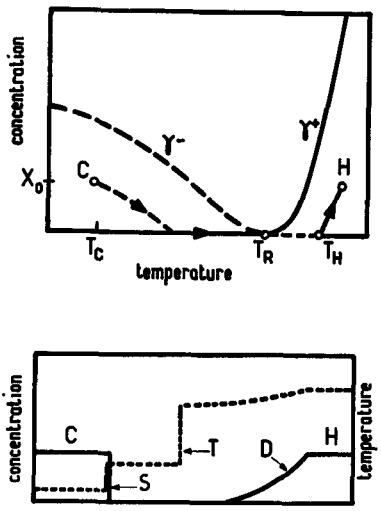

FIG. 5. Top: Traject for a cold step in the (X, T) plane. (- -) γ^-. (——) γ^+. Bottom: X and T equilibrium profiles during a cold step. (——) Concentration. (- -) Temperature.

waves, and above which the reverse is true. Hence the name "reversal temperature." [The point $(X = 0, T = T_R)$ can be called a "watershed point" in the sense defined in multicomponent chromatography (*9*).]

The γ^- originating from a point in Region 1 are entirely contained in that region. Similarly, the γ^+ originating from a point in Region 3 are contained therein. For $T < T_R$, the axis $X = 0$ is a γ^+; and for $T > T_R$, this axis is a γ^-.

USE OF THE (X, T) DIAGRAM FOR THE CONCEPTUAL DESIGN OF A PURIFICATION PROCESS

Consider a column initially completely loaded with a gas of composition X_0 in adsorbable component, and at a temperature T_H high enough for the Point H (X_0, T_H) to be in Zone 3. Without changing the feed composition X_0, let us change the inlet temperature in a single step to T_C, low enough for the point $C(X_0, T_C)$ to be in Zone 1 (cold step). The concentration and temperature distributions generated by this step change in inlet conditions, and connecting conditions H to conditions C, are represented in Fig. 5 (top) for the (X, T) plane and in Fig. 5 (bottom) for the schematic column profile at some arbitrary time.

Three distinct waves may be observed in the column profile, going downstream (from left to right):

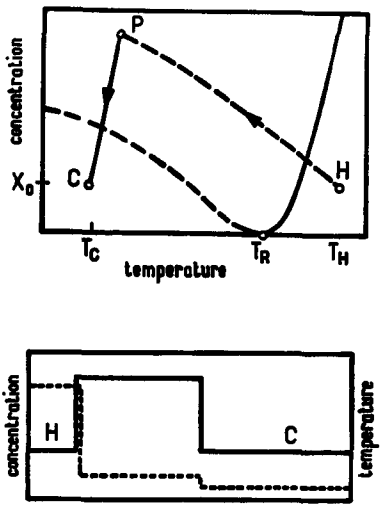

FIG. 6. Top: Traject for a hot step in the (X, T) plane. Bottom: X and T equilibrium profiles during a hot step. (——) Concentration. (- -) Temperature.

A sorption wave S, moving at a velocity which depends only on T_C, not on T_H.

A pure thermal wave T, moving in a region of the column where no adsorbable component is present.

A desorption wave D, moving at a velocity which depends only on T_H, not on T_C.

As this profile moves out of the column, products may be collected. Between the end of the exit of the desorption wave and the beginning of the exit of the sorption wave, the product collected contains no adsorbable component. We have thus separated the adsorbable and nonadsorbable component, but it was not necessary, for doing this, to start from a regenerated column.

Let us now consider the reverse operation. The initial state of the column is represented by C and the inlet feed temperature is made equal to T_H (hot step). Figures 6 (top) and 6 (bottom) show the corresponding traject in the (X, T) plane and the schematic column profile. As this profile moves out of the column, a fraction can be collected which is enriched in adsorbable component.

A process may now be imagined in which a gas of constant composition is fed continuously to a column, and the temperature of the gas at the inlet is changed stepwise between two values T_C and T_H, chosen in such a

way that, at the exit, one may collect in turn a fraction enriched in adsorbable component and a fraction of pure nonadsorbable component. Doing this in an optimal fashion implies that at the outlet of the column only the interesting parts of the profiles emerge. This requires a proper choice not only of the two working temperatures but also of the duration of the cold and hot steps. In the presentation of the experimental results, we show how this choice is made from separate experimental cold and hot steps.

EXPERIMENTAL SET-UP

The experimental results presented in the next section have been obtained with the mixture *n*-pentane/isopentane on a Linde 5 A molecular sieve on which essentially only the *n*-pentane is adsorbed. The column was cylinder of stainless steel, 1 m high and of 10 cm i.d. The wall thickness was 0.8 mm, and a layer of 3 cm glass wool was used as insulation. Temperatures were measured using thermocouples simultaneously at seven locations along the column axis, measurements being recorded every 5 min. Synchronized with these temperature recordings, the effluent composition was measured by gas phase chromatography. At the inlet of the column a heating circuit allowed the temperature of the feed to be adjusted or modified.

FIRST EXPERIMENTAL RESULTS: SEPARATE COLD AND HOT STEP

In all experiments, the pressure inside the column was approximately 1.2 atm and the mass flow rate was 1.9 kg/hr. The column was fed *continuously* with a mixture of *n*-pentane and isopentane containing about 5.7% *n*-pentane. The inlet temperature of the feed varied between 110 and 340°C. For this system, taking into account the heat capacities of the adsorbent, the walls, and the insulation, the reversal temperature T_R can be estimated to be about 270°C.

Figure 7 shows the effluent histories (X% *n*-pentane and T°C) obtained during a cold step: at time $t = 0$ the feed temperature is changed from about 340 to 110°C. Three zones may be observed which correspond to the three zones identified in connection with Fig. 5 (bottom) (note: In Fig. 7 the abscissa is time, in Fig. 5 (bottom) it is distance; the two figures are qualitatively mirror images of each other):

Zone D, where X decreases from 5.7 to 0, and where the temperature varies little.

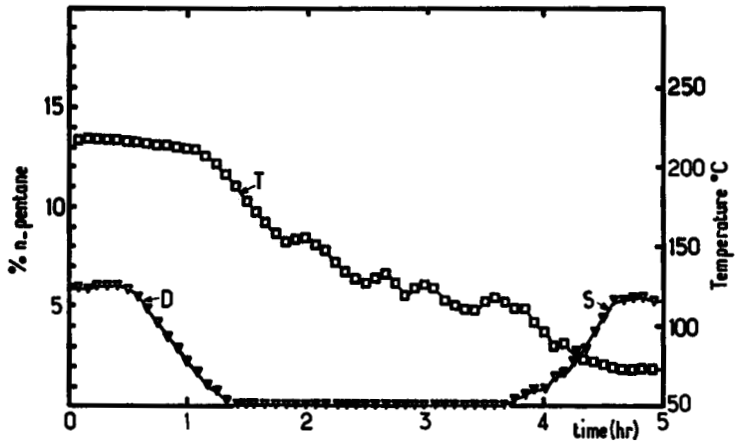

FIG. 7. Experimental concentration and temperature history during a cold step. (▽) *n*-Pentane. (□) Temperature.

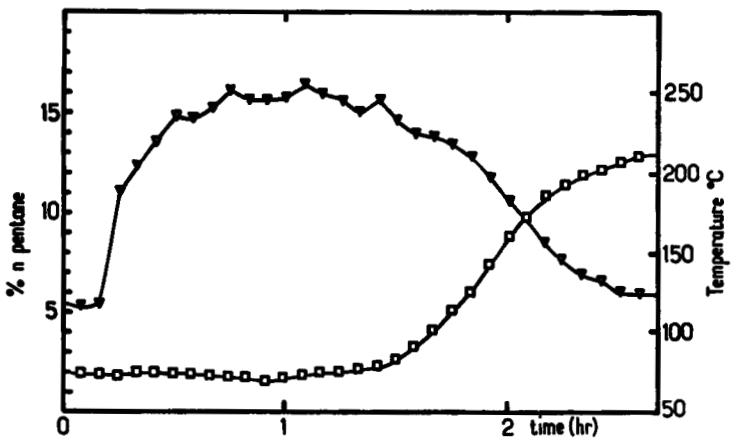

FIG. 8. Experimental concentration and temperature history during a hot step. (▽) *n*-Pentane. (□) Temperature.

Zone *T*, where *X* is zero and the temperature decreases to about 110°C.

Zones *S*, where *X* increases to 5.7 and the temperature decreases to 70°C.

Figure 8 shows the effluent histories obtained during a hot step in which the feed temperature is brought from 110 to 340°C. The curves show the existence of a "plateau" where the *n*-pentane percentage is around or above 16% and the temperature varies little. Then the *n*-pentane per-

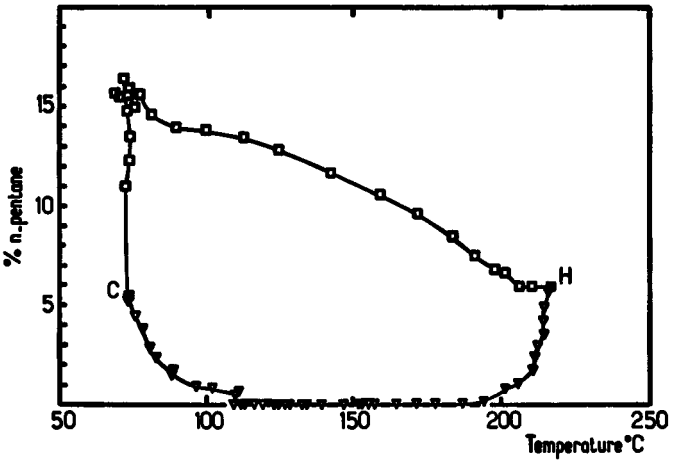

FIG. 9. Representation of separate cold and hot steps (from Figs. 7 and 8) in the (X, T) plane. (∇) Cold step. ($\square$) Hot step.

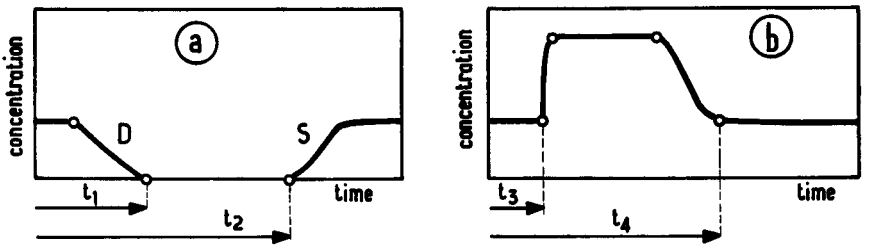

FIG. 10. Determination of the characteristic times for adjustment of the durations θ_C and θ_H of the cold and hot steps in a synchronized cycle. (a) Cold step. (b) Hot step.

centage decreases toward that of the feed while the temperature increases to 220°C. Figure 9 shows the corresponding trajects plotted in the (X, T) plane.

CYCLIC PROCESS

We are now interested in making a succession of cold and hot steps in such way as to produce the desired separation in a cyclic fashion. We must thus chose the durations θ_C and θ_H for the cold and hot steps, respectively. This is done by using characteristic times relative to the separate cold and hot step illustrated before. Figure 10 shows how these times are determined:

t_1: end of exit of desorption wave
t_2: beginning of exit of sorption wave
t_3: beginning of exit of *n*-pentane rich plateau
t_4: end of exit of *n*-pentane rich zone

We now want to synchronize the exit of the sorption wave of a cold step at t_2 with the exit of the sorption wave of the next hot step at $\theta_C + t_3$. This results in

$$\theta_C = t_2 - t_3 \tag{9}$$

Next we want to synchronize the exit of the desorption wave of that hot step at $\theta_C + t_4$ with the exit of the desorption wave of the next cold step at $\theta_C + \theta_H + t_1$. This results in

$$\theta_H = t_4 - t_1 \tag{10}$$

The total cycle time is thus

$$\tau = \theta_C + \theta_H = t_2 + t_4 - t_3 - t_1 \tag{11}$$

In the examples of Figs. 7 and 8, we have

$t_1 = 1$ hr, 20 min; $t_2 = 3$ hr, 40 min; $t_3 = 0$ hr, 10 min;
$t_4 = 2$ hr, 30 min

Therefore, from Eqs. (9), (10), and (11):

$\theta_C = 3$ hr, 30 min; $\theta_H = 1$ hr, 10 min; $\tau = 4$ hr, 40 min

Figure 11 shows the effluent histories (% *n*-pentane and temperature) for an experiment in which the inlet temperature history is the following:

Initial temperature of feed: $T = 340°C$
From $t = 0$ to $t = \theta_C = 3$ hr, 30 min: $T = 110°C$
From $t = 3$ hr, 30 min to $t = \tau = 4$ hr, 40 min: $T = 340°C$

We observe a relatively smooth peak of *n*-pentane, meaning that the sorption waves generated by the cold and hot steps have merged into a combined continuous sorption wave *S*, and similarly the desorption waves have merged into a single desorption wave *D*. The time during which pure isopentane is produced ($X = 0$) is practically identical (2 hr, 25 min) to that observed during the independent cold step.

INFLUENCE OF PHYSICAL FACTORS

The main condition for the process to be applicable is that point (X_0, T_C) be in Zone 1 and point (X_0, T_H) be in Zone 3. These zones are strongly

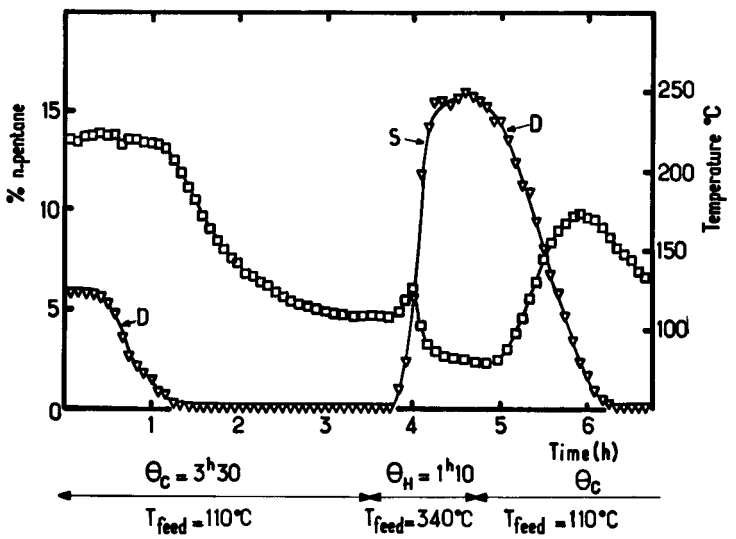

FIG. 11. Experimental concentration and temperature history for the succession of a synchronized cold and hot step. (*S*) Combined sorption wave. (D) Combined desorption wave. (▽) *n*-Pentane. (□) Temperature.

connected to the reversal temperature T_R. The parameters which affect T_R for a given adsorbent and for a given adsorbable component are the specific heat of the nonadsorbable gas and the total pressure. An increase in either or both of these parameters tends to increase T_R and also, for a given T_C, to increase the maximal allowable X_0 for point (X_0, T_C) to remain in Zone 1.

Figure 12 shows the (X, T) diagrams for the system Linde 5A/*n*-pentane with isopentane on the one hand and hydrogen on the other hand as major, nonadsorbable components. It can be seen that in the case of hydrogen, it will be possible to work at lower temperatures since the reversal temperature is lower. On the other hand, Region 1 is much narrower and the maximal impurity concentration is around 3%. Note that if the minor component were less strongly adsorbed (as it would be for lower hydrocarbons), the reversal temperature is also lowered. Thus the process is particularly suitable for the purification of light gases from light impurities.

Figure 13 shows the (X, T) diagrams with H_2 as the major component and *n*-pentane as the minor component for total pressures of 1, 2, and 5 atm. It can be seen that this increase in pressure allows a higher percentage of minor component to be treated but the increase is small, whereas the

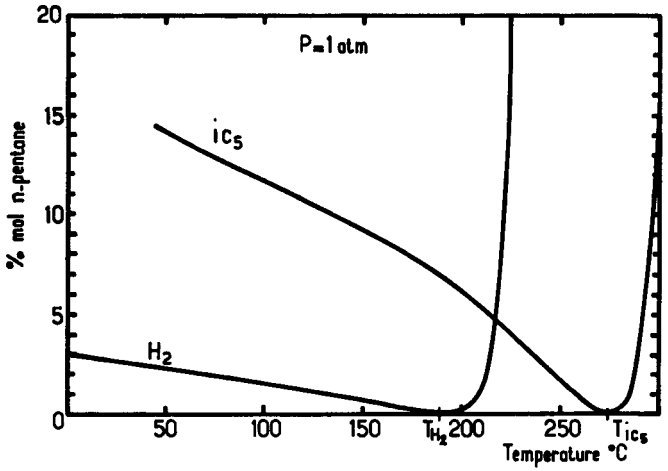

FIG. 12. Influence of nonadsorbable component on the three zones of the (X, T) plane. $T_{H_2} = 190°C$. $T_{IC_5} = 273°C$.

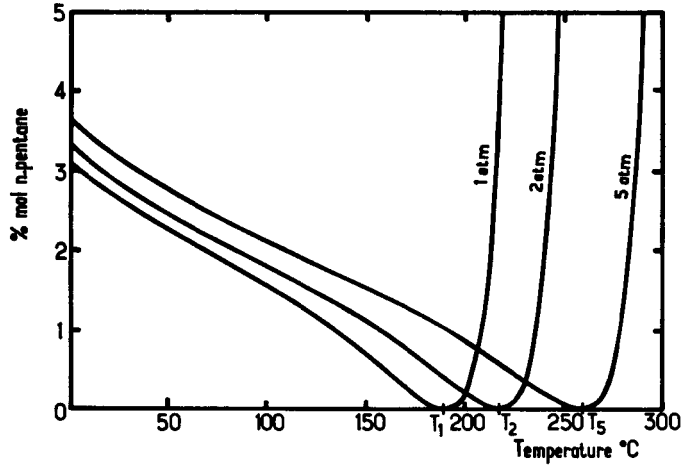

FIG. 13. Influence of total pressure on the three zones of the (X, T) plane system hydrogen/*n*-pentane/Linde 5A. $T_1 = 190°C$. $T_2 = 217°C$. $T_5 = 259°C$.

increase in reversal temperature, i.e., in the high working temperature, is notable. However, we cannot say without further study how general this conclusion is.

POTENTIAL INTEREST OF SUCH PROCESSES

The salient features of the process are the continuous feed, the absence of purge gas (and thus the nondilution of the products with foreign components), and the use of heat as the driving force. It is well suited for the removal of relatively adsorbable minor components in the bulk of nonadsorbed major components and for the recovery of minor components in a nondiluted form. This is important when the minor components are valuable and not condensable at ambient temperature and pressure, and thus not easily recoverable when diluted. For certain systems the working temperatures may turn out to be low, and waste heat can be used as the heat source. The total pressure may be adjusted so that this is possible.

The process can be extended to adsorbable major components and multicomponent mixtures. The technology is simple and may be adapted to any existing plant. At the cost of some sophistication, the minor component can be recovered in a much more concentrated form. This is obtained either by cascading several columns or, more simply, by using part of the minor fraction as feed for the hot step (*8*).

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REFERENCES

1. F. W. Leavitt, *Chem. Eng. Progr.*, *58*, 54 (1962).
2. C. Y. Pan and D. Basmadjian, *Chem. Eng. Sci.*, *25*, 1653 (1970).
3. C. Y. Pan and D. Basmajdian, *Ibid.*, *26*, 45 (1971).
4. H. K. Rhee, E. D. Heerdt, and N. R. Amundson, *Chem. Eng. J.*, *1*, 297 (1970).
5. H. K. Rhee and N. R. Amundson, *Ibid.*, *3*, 122 (1972).
6. R. Courant and D. Hilbert, *Methods of Mathematical Physics*, Vol. II, Wiley-Interscience, New York, 1962.
7. G. Klein, D. Tondeur, and T. Vermeulen, *Ind. Eng. Chem., Fundam.*, *6*, 339 (1967).
8. P. Jacob, Doctoral Thesis, Institut National Polytechnique of Nancy, 1980.
9. F. Helfferich and G. Klein, *Multicomponent Chromatography*, Dekker, New York, 1970.

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