

Sorption of *n*-Alkanes on the Molecular Sieves. II. A Mathematical Model for Desorption

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In this paper a mathematical model is proposed for the desorption of *n*-alkanes from the granulated molecular sieve 5 A which forms a static bed of particles. This model is based on the assumption that the process controlling the exchange of substance is its transport through a gaseous laminar film while the adsorption isotherm is to be described by an equation of straight line.

A theoretical and experimental study of desorption of *n*-alkanes from the granulated molecular sieve 5 A seems to be attractive because of the growing number of factory units for the separation of normal hydrocarbons from a mixture of various structural groups. As stated in the papers [1, 2], the slowest step in these separation processes is the desorption of *n*-alkanes from molecular sieve so that this stage of production cycle is most important from the point of view of the apparatus productivity and process efficiency. Since there is no reason to suppose *a priori* that the resistance against the transport of substance should be essentially greater for desorption than it is for adsorption, the cause of low desorption rate must be due to a low driving force of the process.

The desorption of a substance may be affected:

- a) by temperature raise;
- b) pressure decrease in system;
- c) by flow of inert gas;
- d) by stripping the adsorbate by a desorbent which is adsorbed more firmly than the original adsorbate.

This paper treats the desorption of individual *n*-alkanes from the molecular sieve 5 A by the mode given in item c).

Deduction of partial differential equations describing the desorption of the sorbent particles forming a static bed

The fundamental relationship is the equation of material balance which may be formulated for the differential volume of bed as follows

$$\dot{G}Y \, d\tau = \dot{G} \left[Y + \left(\frac{\partial Y}{\partial Z} \right) dZ \right] d\tau + \varrho_B \, dZ \left(\frac{\partial w}{\partial \tau} \right) d\tau + \varepsilon_G \varepsilon \left(\frac{\partial Y}{\partial \tau} \right) d\tau \, dZ. \quad (1)$$

This equation is sufficiently known in special literature and therefore we think it is not necessary to explain the physical significance of individual terms.

By a simple rearrangement of the equation (1) we get

$$\dot{G}\left(\frac{\partial Y}{\partial Z}\right) = - \left[\varrho_B \left(\frac{\partial w}{\partial \tau}\right) + \varrho_B \varepsilon \left(\frac{\partial Y}{\partial \tau}\right) \right]. \quad (2)$$

Provided the retention of fluid in bed may be neglected in comparison with the volume of fluid which flows through the bed during desorption, the last term in the equation (2) may be neglected. Then this equation gets the form

$$\dot{G}\left(\frac{\partial Y}{\partial Z}\right) = -\varrho_B \left(\frac{\partial w}{\partial \tau}\right). \quad (3)$$

The rate of substance transport is defined by the expression

$$r = k_G a_v (p^* - p). \quad (4)$$

By transforming the equation (4) in which relative fractions are substituted for partial pressures according to the definitions

$$p = \frac{Y M_G}{M_A + M_G Y} \pi,$$

resp. for $Y \ll 1$

$$p = \frac{M_G}{M_A} \pi Y,$$

we obtain

$$r = k_G a_v \pi \frac{M_G}{M_A} (Y^* - Y). \quad (5)$$

The inequality $Y \ll 1$ is practically always fulfilled for the desorption by indifferent gas.

After above transformation, the following equation expresses the time variation of the adsorbate concentration on adsorbent in the course of desorption

$$-\varrho_B \left(\frac{\partial w}{\partial \tau}\right) = r M_A = C(Y^* - Y), \quad (6)$$

where

$$C = k_G a_v \pi M_G. \quad (7)$$

The combination of the equations (3) and (7) provides the system of two partial differential equations

$$-\varrho_B \left(\frac{\partial w}{\partial \tau}\right) = C(Y^* - Y), \quad (8)$$

$$\dot{G}\left(\frac{\partial Y}{\partial Z}\right) = C(Y^* - Y), \quad (9)$$

resp. after rearrangement

$$-\left(\frac{\partial w}{\partial \tau}\right) = b(Y^* - Y), \quad (10)$$

$$\left(\frac{\partial Y}{\partial Z}\right) = a(Y^* - Y), \quad (11)$$

where

$$b = \frac{C}{\rho_B}; \quad a = \frac{C}{\dot{Q}}$$

In the region of the low adsorbate concentration in gaseous phase the adsorption isotherm may be expressed by a straight line equation

$$Y^* = c w. \quad (12)$$

This relationship is always fulfilled for the desorption with a great excess of indifferent gas. If the quantity Y^* in the equations (10) and (11) is expressed by means of the expression (12) we get a system of equations describing the course of adsorption

$$-\left(\frac{\partial w}{\partial \tau}\right) = b c \left(w - \frac{Y}{c}\right), \quad (13)$$

$$\left(\frac{\partial Y}{\partial Z}\right) = a(c w - Y). \quad (14)$$

The form of the equations (13) and (14) is conformable to that of the equations deduced and analytically solved by *Hougen and Marshall* [3] for adsorption. The solution suggested by *Hougen and Marshall* is, however, unapplicable to desorption because of the different formulation of boundary conditions

$$Y(0, \tau) = 0; \quad w(Z, 0) = w_0.$$

We have tried to solve the equations (13) and (14) for these boundary conditions by using analog computer.

Analog model

The system of partial first order differential equations (13) and (14) which describe time, position, and concentration conditions in adsorber may generally be expressed as follows

$$Y = Y(Z, \tau), \quad (15i)$$

$$w = w(Z, \tau). \quad (15ii)$$

The functions (15) express the time-space surfaces represented in Fig. 1. Solution by means of analog computer consists in a division of the adsorber height into sections ΔZ_i , where $Z_i = \text{const}$ and determination of the time dependence of the function (15) for these sections by means of analog computing circuit. The partial derivative with respect to space coordinate is approximated by the difference of two function values in neighbouring intervals [4]

$$\left(\frac{\partial Y}{\partial Z}\right)_{Z_i} \approx \frac{Y_{i+1} - Y_{i-1}}{2\Delta Z}, \quad (16)$$

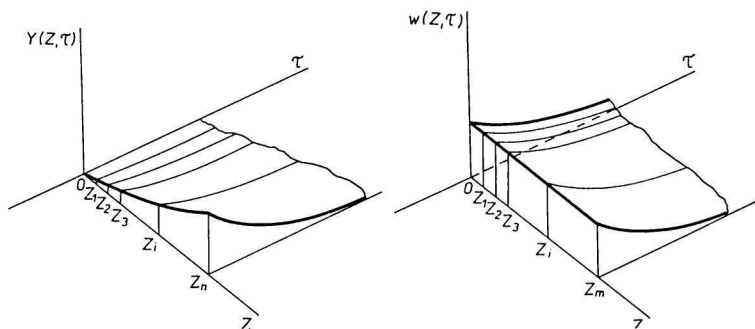


Fig. 1. Time-space surfaces of the functions $Y = Y(Z, \tau)$ and $w = w(Z, \tau)$.

where $\Delta Z = H/n$, n denotes the number of sections of space coordinate and $i = 1, 2, \dots, n - 1$. The equations (13) and (14) are, thus, to be written as follows

$$-w'_i = -\left(\frac{\partial w_i}{\partial \tau}\right)_{Z_i} = b\left(w_i - \frac{Y_i}{c}\right), \tag{17}$$

$$\left(\frac{\partial Y}{\partial Z}\right)_{Z_i} \approx \frac{Y_{i+1} - Y_{i-1}}{2\Delta Z} = a(cw - Y_i). \tag{18}$$

It follows from (18) that

$$Y_i = c w_i - \frac{1}{2a \Delta Z} (Y_{i+1} - Y_{i-1}). \tag{19}$$

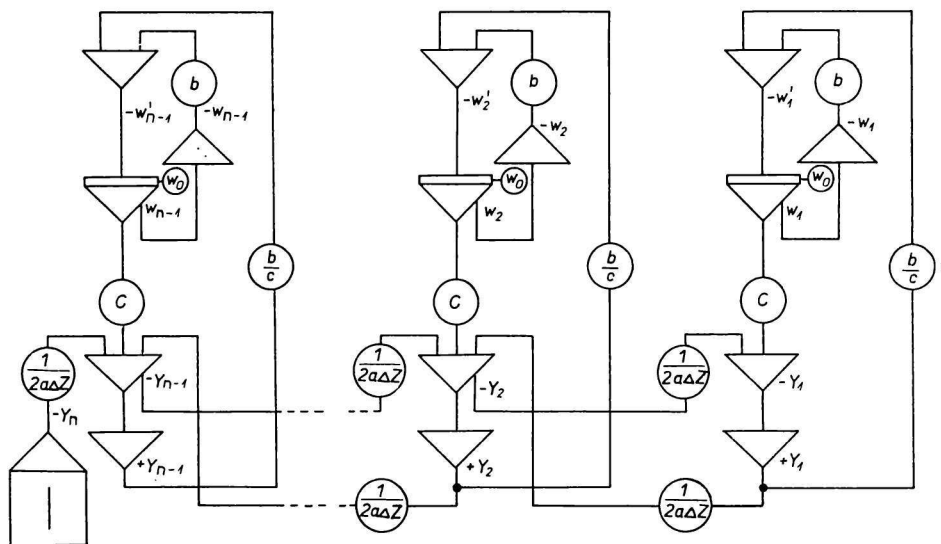


Fig. 2. Programmed scheme of the model equations (17) and (19).

The programmed scheme of the model equations (17) and (19) is shown in Fig. 2. The proposed model enables us to follow the variations $Y(Z, \tau)$ and $w(Z, \tau)$ in different sections of adsorption bed on condition that the course of the function $Y_n(\tau)$, which is to be found by a relatively simple measurement, is known. If the analytical form of the measured relationship $Y_n(\tau)$ is unknown, it must be simulated by a functional transducer. The testing of this model will be described in subsequent paper.

Symbols

a	constant in the equation (11)
a_v	specific surface of the adsorbent particles
b	constant in the equation (10)
c	constant in the equation of adsorption isotherm (12)
C	constant in the equation (6)
G	mass flow of indifferent gas
H	height of adsorption bed
k_G	mass-transport coefficient in the equation (4)
p	partial pressure of adsorbate in the bulk flow of gas
p^*	equilibrium partial pressure of adsorbate
M_A	molecular weight of adsorbate
M_G	molecular weight of indifferent gas
Y^*	equilibrium concentration of adsorbate with respect to p^* (kg of adsorbate per 1 kg of pure indifferent gas)
Y	concentration of adsorbate in the bulk flow of gas (kg of adsorbate per 1 kg of pure indifferent gas)
w	relative weight fraction (kg of adsorbate per 1 kg of adsorbent in the time τ)
w_0	relative weight fraction (kg of adsorbate per 1 kg of adsorbent in the time $\tau = 0$)
ΔZ_i	height of bed section measured in the direction of gas flow
τ	time
ε	porosity
ρ_B	bulk bed density
ρ_G	density of gas
π	total pressure

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