of the diffusing molecule relative to crystal dimensions.

Sorption equilibria must likewise be related to the size and configuration of the sorbed molecules relative to the size of the cavities. Both type A and type Y zeolites have a three-dimensional pore structure consisting of supercavities connected by essentially circular and narrow apertures (5 Å and 9 Å, respectively), but the structural dimensions of the two zeolites are different and it is not apparent why dodecane should be able to take up a relatively more favored packing arrangement in both zeolites. We can visualize that the higher weight molecule finds its most favorable packing while the smaller molecule takes up the remaining space which it can do more readily because it is smaller. A dip in value of γ_H then represents a case in which the hydrocarbon molecule can fit well into a cavity or multiple of cavities as opposed to other hydrocarbon structures in which the molecule cannot achieve full packing in a cavity or must spread itself through more than one cavity, leaving substantial free space. Extending these studies to other paraffin systems could permit a more quantitative approach to prediction based on the known structure of zeolite pore systems and paraffin molecules.

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On Inventory Times in Approximate Dynamic Distillation Modeling

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In recent years Williams and his colleagues have devised methods for constructing approximate mathematical models of unsteady distillation column operation on the basis of a time constant called the inventory time (Moczek et al., 1965; Bhat, 1969; Bhat and Williams, 1969; Weigand et al., 1972). Their objective has been to develop models that use only steady state information and which are simple enough to be used, with periodic updating if necessary, for feedforward control. The methods are reasonably successful in the sense that adequate approximate models are obtained in suitable cases. The models are not required to be predictive in all cases, for it is possible to check the approximate model by comparison with a more precise model before it is used in the design of a control system. Weigand et al. (1972) have presented such comparisons for several distillation types.

Inventory times are defined in terms of steady state compositions and flow rates and have been shown by Williams and his co-workers to be related to the time constants of the response of a distillation column to disturbances in operation. For example, if the response to an upset in the feed is slow in one product stream and fast in the other, the inventory time is the sum of the time constants for the slower response (Moczek et al., 1965). Inventory times bear a strong resemblance to mean residence times as defined by Buffham and Kropholler (1973) for steady operation of complex flow networks. In this note it is shown that corresponding parameters can be defined for each species present in a distillation process without reference to the details of a mathematical model of the distillation process.

The simplest case of a mean residence or response time is Danckwerts' (1953) familiar result that the mean residence time for steady single-phase flow in a constant-volume mixing vessel is

$$\tau = \text{volume/flow rate}$$

For more complex configurations this becomes (Buffham and Kropholler, 1973)

$$\tau_i = \frac{\text{holdup of species } i}{\text{throughput of species } i}$$

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Bhat and Williams (1969) describe their inventory time as

$$T_{\text{INV}} = \frac{\text{total change in storage for the whole column}}{\text{total change in flow out of whole column}}$$

where it is understood that reference is made to a particular species and that the transient in question is evolution from one steady state to another in response to a step change. It should be noted that the change in flow is actually that change which occurs after the initial rapid hydraulic transient. They also derived modified inventory times from a column material balance.

The mean time and the inventory time are sufficiently similar in appearance to suggest that modified inventory times can be derived in a similar way to the mean residence time, thus avoiding the assumptions in Bhat and Williams' analysis. A material balance is integrated by parts, noting that the *uv* term may be expressed in terms of steady states.

Consider a distillation column processing a single multicomponent feed to produce a distillate and a bottom product. A material balance on the *i*th species yields

$$\int_0^t (Fx_F - Bx_B - Dx_D)dt = H_i(t) - H_i(0) \qquad (1)$$

where F, B, and D are molar flow rates of feed, bottoms, and distillate streams containing mole fractions x_F, x_B, and x_D of the *i*th species, and H_i is the total holdup of that species within the column, associated reboiler, and condenser. Integrating by parts,

$$[(Fx_F - Bx_B - Dx_D)t]_0^t - \int_0^t t\frac{d}{dt}(Fx_F - Bx_B - Dx_D)dt = H_i(t) - H_i(0) \qquad (2)$$

For a transient between two steady states, $Fx_F - Bx_B - Dx_D = 0$ at both $t = 0$ and $t = \infty$. In order for the integral in Equation (1) to be finite as the steady state is approached, $|Fx_F - Bx_B - Dx_D|$ must decay faster than t^{-1} so that we have the stronger condition that $(Fx_F - Bx_B - Dx_D)t$ tends to zero as the final steady state is approached. This ensures that the first term in Equation (2) makes no contribution for a transient between steady states. For a step response $t\ d(Fx_F)/dt = 0$ so that Equation (2) becomes

$$\int_0^\infty t\frac{d}{dt}(Bx_B + Dx_D)\ dt = H_i(\infty) - H_i(0) \qquad (3)$$

In distillation, hydraulic transients are rather more rapid than product-composition transients. Let us assume that this separation in time is so distinct that

$$\begin{aligned} x_B &= x_B(0) = x_{B0} && \text{when} \quad dB/dt \neq 0 \\ B &= B(\infty) = B_\infty && \text{when} \quad dx_B/dt \neq 0 \\ x_D &= x_D(0) = x_{D0} && \text{when} \quad dD/dt \neq 0 \\ D &= D(\infty) = D_\infty && \text{when} \quad dx_D/dt \neq 0 \end{aligned}$$

Equation (3) then becomes, on differentiating the products Bx_B and Dx_D,

$$x_{B0}\int_0^\infty t\frac{dB}{dt}dt + x_{D0}\int_0^\infty t\frac{dD}{dt}dt + B_\infty\int_0^\infty t\frac{dx_B}{dt}dt + D_\infty\int_0^\infty t\frac{dx_D}{dt}dt = H_i(\infty) - H_i(0) \qquad (4)$$

The integrals here represent the area between $B(t)$ and its asymptote $B(\infty)$ etc., and consequently Equation (4) may be expressed

$$x_{B0}(B_\infty - B_0)\ \tau_B{}^H + x_{D0}(D_\infty - D_0)\ \tau_D{}^H + x_{B\infty} - x_{B0})B_\infty\tau_B + (x_{D\infty} - x_{D0})D_\infty\tau_D = H_i(\infty) - H_i(0) \qquad (5)$$

where $\tau_B{}^H$, $\tau_D{}^H$ are time constants relating to the hydraulic transients and τ_B and τ_D refer to the composition transients for species i. Usually the curves $B(t), \ldots, x_D(t)$ will be sigmoidal and the derivatives bell shaped so that the time constants may be regarded as mean times for the transients. For linear responses, $(B_\infty - B_0)^{-1}\ dB/dt$ is the impulse response and τ_B the mean time in the usual sense, and similarly for the other variables. If, following Bhat and Williams, we assume that the hydraulic transients are very rapid:

$$(x_{B\infty} - x_{B0})B_\infty\tau_B + (x_{D\infty} - x_{D0})D_\infty\tau_D = H_i(\infty) - H_i(0) \qquad (6)$$

By adding $(x_{B\infty} - x_{B0})B_\infty\ (\tau_D - \tau_B)$ to both sides and rearranging,

$$\tau_D = \frac{H_i(\infty) - H_i(0) + (x_{B\infty} - x_{B0})B_\infty\ (\tau_D - \tau_B)}{(x_{B\infty} - x_{B0})B_\infty + (x_{D\infty} - x_{D0})D_\infty} \qquad (7a)$$

and, similarly,

$$\tau_B = \frac{H_i(\infty) - H_i(0) + (x_{D\infty} - x_{D0})D_\infty\ (\tau_B - \tau_D)}{(x_{B\infty} - x_{B0})B_\infty + (x_{D\infty} - x_{D0})D_\infty} \qquad (7b)$$

Equations (7) are equivalent to Equations (8) of Weigand et al. (1972) for the modified inventory time, but include vapor-phase holdup and apply to multicomponent operation of any type of column. Properly constructed mathematical models of column behavior automatically satisfy Equation (3) and, in appropriate circumstances, its subforms because material balances will have been incorporated for each species when the model was formulated. On the other hand, these relations may be used to eliminate one parameter for each species present from empirical models in which material balances are not specified.

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