

NONSTATIONARY PHASE FLOW AND RECTIFICATION
ACCELERATION IN INDUSTRIAL PLANT

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A new rectification method has been implemented on a large scale that has low energy consumption and provides improved quality in the distillate and improved throughput. The optimum parameters may be calculated from a liquid-vapor mass-transfer model, for which an analytic solution exists.

Separations are the most uneconomical processes in chemical engineering; the efficiency in heat use in rectification is only 5-10% [1]. There are no universal recommendations for reducing the energy consumption in rectification plant. The energy consumption can be reduced by optimizing the irrigation (only by maintaining the optimum phlegm number), but the change is of the same order as from the replacement of contact devices: up to 13%.

Cyclic flow organization is a relatively new concept for accelerating processes in chemical engineering. Cannon [2, 3] published the first papers on cyclic processes in the mid-1950s, and there and in subsequent papers of experimental type, it was found that cyclic methods can be applied in rectification, solvent extraction, crystallization, and so on [4, 5].

The cyclic method involves supplying the contacting phases in turn at set intervals; the method has attracted attention and has considerable scope for improvement. The first researches on cyclic rectification [5, 6] showed increases in throughput and performance by factors of 2-3. The control is highly flexible, because the phase supply times are adjustable.

These advantages of cyclic rectification and absorption are of industrial significance, but [7, 8] reduced optimism. Adverse effects were observed: poor controllability in any column with more than 10-12 plates because of inertia in the vapor flow, while in a column with gridded plates of large diameter, there was no improvement in performance.

There are many theoretical papers on cyclic processes [7, 9-11]; the cybernetics department at Mendeleev Moscow Chemical Engineering Institute has collaborated with the Ufa synthetic alcohol plant for more than 10 years in developing and implementing large-scale rectification by the new method, which differs from the [7, 8] methods and is carried out in bubble-plate columns (gridded, capped, or valve types) with overflow. The raw material and the residue are supplied to the column in a strictly defined fashion, whose parameters are dependent on the column working conditions and mixture properties.

The method can be realized in existing rectification columns without changes in design, technology, or control system; the supply lines for the residue and the raw material are fitted with pneumatic valves having membrane-type pneumatic drives, which receive the cycling signals of appropriate form. The cycling signal generator can be provided by a microcomputer, microcontroller, and so on in conjunction with an electropneumatic valve. The liquid flowing from plate to plate as a flow of residue and raw material comes in contact with the vapor rising from the lower plates. The alternation of maximal and minimal liquid flow speeds through the plates has a strictly defined relationship to the cycle time and is determined by solving equations describing the transient mass transfer.

MASS-TRANSFER MODEL FOR NONSTATIONARY VAPOR-LIQUID FLOWS

The mass transfer involves nonstationary vapor-liquid flows in the plates and was described by means of a diffusion model for the liquid phase and a complete-mixing one for the vapor.

The equation system is

$$\begin{aligned} \frac{\partial x}{\partial t} &= \frac{D}{l^2} \frac{\partial^2 x}{\partial z^2} - \frac{\omega}{l} \frac{\partial x}{\partial z} - K_{0x} \left(x - \frac{y}{m} \right), \\ \frac{\partial y}{\partial t} &= \frac{G}{V} (y_0 - y) + K_{0x} \left(x - \frac{y}{m} \right). \end{aligned} \quad (1)$$

Boundary conditions:

$$D \frac{\partial x}{\partial z} \Big|_{z=0} = \omega [x(t, 0) - x_0(t)], \quad \frac{\partial x}{\partial z} \Big|_{z=1} = 0.$$

Initial conditions:

$$x(0, z) = \varphi_1(z), \quad y(0, z) = \varphi_2(z).$$

System (1) with the boundary and initial conditions may be solved analytically; for convenience, we eliminate the first derivative with respect to the spatial variable, for which we make the changes in variables:

$$x - x_0(t) = \exp\left(-\frac{\omega}{2D}z\right) x_1, \quad y - y_0(t)m = \exp\left(-\frac{\omega}{2D}z\right) y_1;$$

which gives a new system

$$\begin{aligned} \frac{\partial x_1}{\partial t} &= \frac{D}{l^2} \frac{\partial^2 x_1}{\partial z^2} - \mu_{11}x_1 + \mu_{12}y_1, \quad \frac{\partial y_1}{\partial t} = \mu_{12}x_1 - \mu_{22}y_1 + f_1(z), \\ \frac{\partial x_1}{\partial z} \Big|_{z=0} &= \beta_1 x_1 \Big|_{z=0}, \quad \frac{\partial x_1}{\partial z} \Big|_{z=1} = \beta_2 x_1 \Big|_{z=1}, \\ x_1(0, z) &= \varphi_{11}(z), \quad y_1(0, z) = \varphi_{21}(z), \end{aligned} \quad (2)$$

in which

$$\begin{aligned} \varphi_{11}(z) &= \exp\left(-\frac{\omega l}{2D}z\right) \{\varphi_1(z) - x_0(0)\}, \\ \varphi_{21}(z) &= \exp\left(-\frac{\omega l}{2D}z\right) \{\varphi_2(z) - x_0(0)\}, \\ f_1(z) &= \frac{G}{V} \exp\left(-\frac{\omega l}{2D}z\right) \{y_0 - x_0(0)m\}, \quad \beta_1 = -\beta_2 = \frac{\omega l}{2D}, \\ \mu_{11} &= \frac{\omega^2}{4D} + K_{0x}, \quad \mu_{12} = \frac{K_{0x}}{m}, \quad \mu_{21} = K_{0x}, \quad \mu_{22} = \frac{K_{0x}}{m} + \frac{G}{V}, \end{aligned}$$

with ω the linear speed of the liquid in m/sec, l liquid path length, D reverse mixing coefficient in m^2/sec , G vapor flow rate in kmol/h , V vapor volume in m^3 , K_{0x} the volume mass transfer coefficient in $\text{kmol}/m^3 \cdot \text{h}$, and m the slope of the equilibrium line. The solution $x_1(t, z)$ and $y_1(t, z)$ to (2) is derived as Fourier series:

$$x_1(t, z) = \sum_{n=1}^{\infty} x_n(z) T_{nx}(t), \quad y_1(t, z) = \sum_{n=1}^{\infty} x_n(z) T_{ny}(t) \quad (3)$$

in terms of the eigenfunctions $x_n(z)$, $n = 1, 2, \dots$, for the boundary-value problem

$$D \frac{\partial^2 x}{\partial z^2} + \lambda l^2 x = 0, \quad \frac{\partial x}{\partial z} \Big|_{z=0} = \beta_1 x \Big|_{z=0}, \quad \frac{\partial x}{\partial z} \Big|_{z=1} = \beta_2 x \Big|_{z=1}. \quad (4)$$

Let λ_n , $n = 1, 2, \dots$, denote the eigenvalues for (4), whereupon $\kappa_n^2 = \lambda_n l^2 / D$ obeys

$$\text{tg } \kappa_n = \frac{2\beta_1 \kappa_n}{\kappa_n^2 - \beta^2}, \quad (5)$$

which corresponds to a sequence of values for the κ_n

$$0 < \kappa_1 < \kappa_2 < \kappa_3 < \dots$$

The normalized eigenfunctions $x_n(z)$ corresponding to the eigenvalues λ_n are

$$x_n(z) = K_n (\beta \sin \kappa_n z + \kappa_n \cos \kappa_n z), \quad (6)$$

in which

$$K_n = \left[\beta + 0,5(\beta^2 + \kappa_n^2) \right]^{-\frac{1}{2}}.$$

We expand the functions $f_1(z)$, $\phi_{11}(z)$, and $\phi_{21}(z)$ in terms of the orthonormalized system of $x_n(z)$:

$$f_1(z) = \sum_{n=1}^{\infty} f^n x_n(z), \quad \phi_{11}(z) = \sum_{n=1}^{\infty} \phi_n^1 x_n(z), \quad \phi_{21}(z) = \sum_{n=1}^{\infty} \phi_n^2 x_n(z),$$

to get a system of ordinary differential equations for the functions $T_{nx}(t)$ and $T_{ny}(t)$:

$$\begin{aligned} \frac{\partial T_{nx}}{\partial t} &= -\lambda_n T_{nx} - \mu_{11} T_{nx} + \mu_{12} T_{ny}, \\ \frac{\partial T_{ny}}{\partial t} &= \mu_{21} T_{nx} - \mu_{22} T_{ny} + f^n, \\ T_{nx}(0) &= \phi_n^1, \quad T_{ny}(0) = \phi_n^2. \end{aligned} \quad (7)$$

For each $n = 1, 2, \dots$, the solution is provided by the following functions:

$$T_{nx}(t) = \frac{\mu_{22} + v_{1n}}{\mu_{21}} C_{1n} \exp(v_{1n}t) + \frac{\mu_{22} + v_{2n}}{\mu_{21}} C_{2n} \exp(v_{2n}t) + \frac{f^n \mu_{12}}{\mu_{22}(\lambda_n + \mu_{11}) - \mu_{21}\mu_{12}}, \quad (8)$$

$$T_{ny}(t) = C_{1n} \exp(v_{1n}t) + C_{2n} \exp(v_{2n}t) + \frac{\lambda_n + \mu_{11}}{\mu_{12}} \frac{f^n \mu_{12}}{\mu_{22}(\lambda_n + \mu_{11}) - \mu_{21}\mu_{12}}, \quad (9)$$

in which v_{1n} and v_{2n} are the roots of

$$(\lambda_n + \mu_{11} + v)(\mu_{22} + v) - \mu_{21}\mu_{12} = 0, \quad (10)$$

while the constants C_{1n} and C_{2n} are given by

$$\begin{aligned} \frac{\mu_{22} + v_{1n}}{\mu_{21}} C_{1n} + \frac{\mu_{22} + v_{2n}}{\mu_{21}} C_{2n} + \frac{f^n \mu_{12}}{\mu_{22}(\lambda_n + \mu_{11}) - \mu_{21}\mu_{12}} &= \phi_n^1, \\ C_{1n} + C_{2n} + \frac{\lambda_n + \mu_{11}}{\mu_{21}} \frac{f^n \mu_{12}}{\mu_{22}(\lambda_n + \mu_{11}) - \mu_{21}\mu_{12}} &= \phi_n^2. \end{aligned} \quad (11)$$

As $\mu_{11}\mu_{22} - \mu_{21}\mu_{12} > 0$, both roots of (10) are negative.

The coefficients f^n are given by

$$f^n = b \frac{2\beta_1 \kappa_n}{\kappa_n^2 + \beta_1^2} K_n, \quad (12)$$

in which $b = G/V(y_0 - x_0m)$.

The mean vapor concentration at the outlet from a plate is

$$y_1(t) = \sum_{n=1}^{\infty} \exp(\beta_1 t) \sin \kappa_n T_{ny}(t). \quad (13)$$

In turn, the mean value of $y_1(t)$ over a time interval ΔT is given by

$$\frac{1}{\Delta T} \int_0^{\Delta T} T_{ny}(t) dt = \frac{\lambda_n + \mu_{11}}{\mu_{12}} \frac{f^n \mu_{12}}{\mu_{22}(\lambda_n + \mu_{11}) - \mu_{21}\mu_{12}} + C_{1n} \frac{\exp(v_{1n}\Delta T) - 1}{\Delta T v_{1n}} + C_{2n} \frac{\exp(v_{2n}\Delta T) - 1}{\Delta T v_{2n}}.$$

Any change in liquid speed at a plate alters the $x_n(z)$ in (4), so when we consider periodic liquid motion over the plates with period T , the liquid moves with speed ω_1 (maximum value) for time $t_1 = T/C$, in which C is the mark-space ratio, while for time $t_2 =$

$T(C - 1)/C$, it moves with speed ω_2 (minimum value) followed by repetition. The concentration profile for the phase flows can be calculated at times that are multiples of t_1 and t_2 by converting in (3) from the $x_n(z, \omega_1)$ function system corresponding to ω_1 , $i = 1, 2$, to the system $x_n(z, \omega_{3-i})$, corresponding to ω_{3-i} , $i = 1, 2$.

The coefficients in the expansion of any function with respect to those systems are

$$h(z) = \sum_{i=1}^{\infty} \alpha_n x_n(z, \omega_1) = \sum_{i=1}^{\infty} \beta_n x_n(z, \omega_2)$$

and are related by a transition matrix a_{kn} , whose elements are given by

$$a_{kn} = \frac{1}{2(K_n')^2} \left\{ \frac{\beta_1 \beta_1' + \kappa_k \kappa_n'}{(\kappa_k - \kappa_n')^2 + \beta_0^2} \{ \beta_0 \exp(\beta_0) \cos(\kappa_k - \kappa_n') - \beta_0 + \right. \\ \left. + (\kappa_k - \kappa_n') \exp(\beta_0) \sin(\kappa_k - \kappa_n') \} + \frac{\kappa_k \kappa_n' - \beta_1 \beta_1'}{(\kappa_k + \kappa_n')^2 + \beta_0^2} \{ \beta_0 \exp(\beta_0) \times \right. \\ \left. \times \cos(\kappa_k + \kappa_n') - \beta_0 + (\kappa_k + \kappa_n') \exp(\beta_0) \sin(\kappa_k + \kappa_n') \} + \right. \\ \left. + \frac{\beta_1 \kappa_n' + \beta_1' \kappa_k}{(\kappa_k + \kappa_n')^2 \beta_0^2} \{ \beta_0 \exp(\beta_0) \sin(\kappa_k \kappa_n') - (\kappa_k + \kappa_n') \times \right. \\ \left. \times \exp(\beta_0) \cos(\kappa_k + \kappa_n') + (\kappa_k + \kappa_n') \} + \frac{\beta_1 \kappa_n' - \beta_1' \kappa_k}{(\kappa_k - \kappa_n')^2 + \beta_0^2} \times \right. \\ \left. \times \{ \beta_0 \exp(\beta_0) \sin(\kappa_k - \kappa_n') - (\kappa_k - \kappa_n') \exp(\beta_0) \cos(\kappa_k - \kappa_n') + (\kappa_k - \kappa_n') \} \right\},$$

in which the primed symbols correspond to the system with liquid speed ω_2 and the unprimed ones to ω_1 :

$$\beta_0 = \beta_1 - \beta_1', \quad \alpha_n = \sum_{k=1}^{\infty} a_{nk} \beta_k, \quad \beta_n = \sum_{k=1}^{\infty} a_{nk} \alpha_k.$$

An algorithm has been devised to give the optimum parameters (T_{opt} , $\omega \pm \Delta\omega$) for the rectification, which is represented by the Fig. 1 block diagram.

I. The stationary state is considered (it is assumed that the system is in that state with liquid speed ω_0 at the start) for the model composed above: 1) one calculates the κ_{ni} from (3)-(5); 2) one calculates the values of the $x_n(z)$ from (6); 3) one calculates the f^n

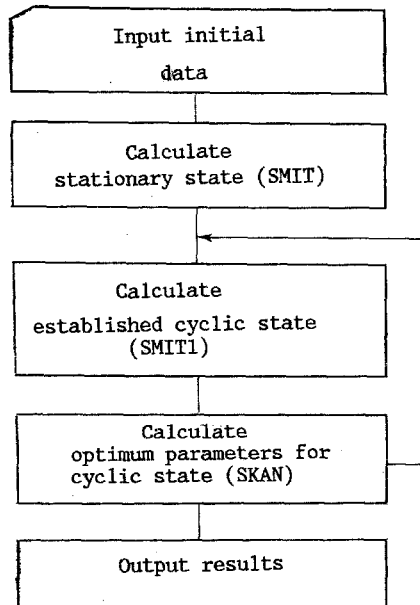


Fig. 1. Block diagram of algorithm for calculating the optimum parameters in nonstationary rectification.

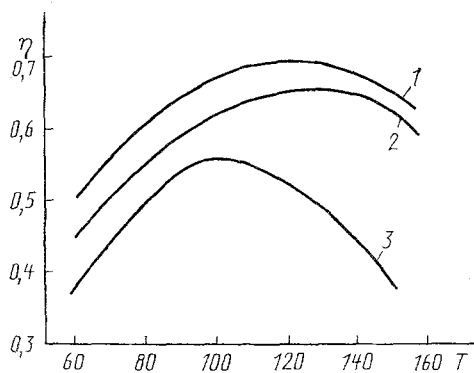


Fig. 2. Plate efficiency η as a function of period T in sec for various oscillation amplitudes: 1) $\Delta\omega = 0.122$ m/sec; 2) 0.114; 3) 0.106.

from (11); 4) one calculates the $T_{nx}(t)$ and $T_{ny}(t)$ from (8)-(11), with the set T_{nx}^0 , T_{ny}^0 specified for ω_0 ; and 5) one calculates the vapor concentration at the exit from a plate $y_1(t)$ from (13), in which $T_{ny}(t) = T_{ny}^0$, and then the plate efficiency.

II. The calculations on the cyclic state are based on the results obtained for the stationary state: 6) one calculates the a_{kn} to convert from ω_0 to ω_1 and onward to ω_2 ; 7) one calculates new values for the $x_n(z)$ on the basis of the a_{kn} ; 8) one calculates new values for the T'_{nx} and T'_{ny} ; and 9) one calculates the vapor concentration at the plate exit and the plate efficiency.

III. The optimal parameters are calculated from the SMIT1 subroutine by two-dimensional scanning; the optimized parameters were the cycle period T and the oscillation amplitudes for the input and residue.

We chose a column for separating acetone-water mixtures in large-scale phenol-acetone production. Figure 2 shows the variation in plate efficiency with T and the residue oscillation amplitude. The best separation performance with the optimal cycle parameters corresponds to minimum vapor flow rate in the boiler in the existing column. This enables one to judge how well the model fits the actual separation and the scope for using it in design calculations and in deriving the optimum parameters.

The conclusions are:

1. A new rectification method has been devised, which reduces the power consumption and increases the column throughput when the user requires improved quality in the distillate or residue, and also improves the quality of the target product without additional capital investment consequent on increasing the number of plates or changing the type.

2. A mass-transfer model has been formulated that incorporates the periodic liquid supply, which enables one to use it in design calculations and also to determine the optimum parameters.

3. The method has been used for a long period under industrial conditions with rectification columns producing: a) commercial acetone, where the vapor flow rate in the boiler has been reduced by 24-33% (from 10.5 to 7-8 tons/h); b) commercial phenol, by 18% (from 11 to 9 tons/h); and c) in isolating butylene-divinyl fractions, by 25.3% (from 1.66 to 1.24 tons/h), where the heavy-hydrocarbon content in the distillate was reduced from 0.8 to 0.4%, while the throughput without choking in the column was increased from 5 to 7 tons/h (in the production of concentrated ethylene).

4. The method is simple to implement and rapidly pays for itself with existing heavy energy-consuming columns in the chemical, petrochemical, and related industries, where it reduces the energy demand considerably and increases the capacity with minimal capital investment.

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FERMENTATION-MEDIUM RHEOLOGY IN ANTIBIOTIC PRODUCTION

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Measurements have been made on the rheological characteristics of antibiotics under industrial conditions; a power-law relationship applies closely. Maxima occur in the consistency index and minima in the rheological index as the fermentation develops.

Many difficulties in designing and managing biological processes are due to the rheologically complicated behavior of fermentation media, as fibrous microorganisms are present even at low biomass concentrations, and they result in highly viscous and usually non-Newtonian suspensions. It has repeatedly been shown [1-17] that mycella suspensions show non-Newtonian behavior. In a fermentation, the rheological features vary because the mycella concentration alters, as do the morphological characteristics [1]. The data in the literature accessible to us on this are inadequate [1-4]. A major problem in such research concerns the reproducibility between cycles.

When rheological characteristics are measured with normal viscometers such as concentric cylinders, there are difficulties [5] arising from the sizes of the particles, which are comparable with the gap between the cylinders, which means that the structures are disrupted by the measurements; it is also possible for lower-density layers to form at the wall, which makes the results doubtful; the suspensions may also precipitate.

To eliminate these difficulties, it has been proposed to use a 6-blade [1, 5, 6] or 8-blade [7] propeller stirrer or spiral strip [13], which is coupled to the electromechanical part of a standard rotational viscometer. Also, one can assume to $\pm 20\%$ that the shear rate is a simple function of the speed and is independent of the rheological properties [18, 19]. The apparatus has however to be calibrated, which is done by the method given by Metzner and Otto [18] as developed in [1, 6] to suit the rheology. A deficiency is the comparatively narrow range in which the flow is laminar, which is particularly important for low-viscosity liquids.

Surveys [2, 8, 9, 20] deal with fermentation-medium rheology; Table 1 gives the main results from those sources and additional ones in recent years.

Even for a single species of microorganism such as *Penicillium chrysogenum*, there are various possible rheological models [1, 2, 4, 5, 10, 11], which is largely related to the shear rate range used, since the models are basically experimental ones, not theoretical flow laws. In a sufficiently narrow shear rate range, all those models gives satisfactory accuracy [1, 2, 4] (Fig. 1). As the descriptions are similar in accuracy, the model is chosen on the basis of simplicity.

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