

# Derivation of Transfer Functions for Highly Nonlinear Distillation Columns

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One of the major problems in distillation column control is obtaining a suitable linear transfer function model for columns that are highly nonlinear and complex. Neither analytical nor numerical linearization methods work well for realistically complex distillation systems. Identification techniques, such as pulse testing, also become ineffective when the columns are highly nonlinear or have large time constants. A simple, easy-to-use design procedure is presented that appears to work quite well on these systems. The method uses Astrom's "autotune" method (relay feedback) to get critical gains and frequencies for each diagonal element of the plant transfer function matrix. Only  $N$  tests are required for an  $N \times N$  multivariable process. Steady-state gains are obtained in the normal way, using a steady-state "rating" program. Then all  $N \times N$  transfer functions are obtained by fitting the zero frequency and ultimate frequency data. The effectiveness of the method is illustrated on a highly nonlinear distillation column that features product purities of 10 ppm.

One of the major unanswered questions in distillation column modeling and control is how to obtain a suitable linear transfer function model for columns that are highly nonlinear. Since almost all control analysis and synthesis techniques use linear process models, it is very important to be able to obtain an appropriate transfer function representation that will yield an effective and robust control system. This is particularly true in multivariable processes where a large number ( $N \times N$ ) of transfer functions must be found.

Nonlinearity can arise because of complex processing configurations (e.g., prefractionators, sidestreams, and multiple feeds) or from nonideal vapor-liquid equilibrium (VLE). However, nonlinearity occurs most frequently in distillation because of high product purities. As purity levels increase above the 98% level, the response of the system becomes highly nonlinear (Fuentes and Luyben, 1983; Marlin et al., 1986).

If the distillation system is simple (binary and equimolar overflow), the nonlinear ordinary differential equations describing the dynamic system can be linearized analytically and an accurate linear model can be obtained. The "stepping technique" of Lamb and Rippin (Luyben, 1973) gives frequency response results for the process open-loop transfer functions. These analytically derived linear models were shown to work quite well for even very high purities (down to 10 ppm impurity) by Fuentes and Luyben (1983).

However, analytical linearization becomes very complex when more realistic distillation systems are studied: multicomponent, nonideal VLE, nonequimolar overflow, inefficient trays, multiple feeds, and sidestreams. Attempts to use numerical linearization (making small changes in each variable and reevaluating the derivatives) have usually been unsuccessful because of the dimensionality of the problem and the high degree of nonlinearity.

Many engineers use the procedure of trying to get transfer function models from either plant tests or from a rigorous nonlinear model of the column. The latter is often very useful, even when plant data are available, for pretesting alternative control schemes before trying them on the plant.

If the column is being designed, most of the information needed to derive a mathematical model of the column is usually available from the column designer (steady-state

conditions, physical dimensions, VLE, and physical property correlations). Steady-state plant data can be used from an existing column to back-calculate actual parameters (tray efficiencies, heat-transfer coefficients, etc.). The only additional information needed to develop a rigorous dynamic model is liquid holdups on trays and in the reflux drum and column base. Therefore it is relatively easy to simulate the rigorous nonlinear column.

By use of either the plant or a rigorous model, an appropriate steady state is established. Then some experimental identification procedure, like pulse testing, is used in an attempt to determine a linear transfer function model. With all loops on manual, one input is changed and its effects on all outputs are recorded. This is repeated for each input.

However, difficulties immediately arise for very nonlinear columns. Very large changes occur in the calculated transfer functions as the size or direction of the input disturbance is changed. Sometimes extremely small magnitude changes (less than 0.01%) have to be made in order to get accurate transfer function parameters. This immediately rules out the use of real plant data because they are never known to anywhere near this order of accuracy. Even with a computer simulation using double-precision calculations, results are frequently quite unreliable. The more nonlinear the column, the greater the problem.

After struggling with this problem for many years, we have finally developed a procedure that is relatively simple and has the potential to be very useful. The objective of this paper is to present the procedure and to illustrate its effectiveness on one specific, very nonlinear distillation column using computer simulation. The procedure has been used very successfully on several other columns.

## Results of a Recent Study

The concept has grown out of the results of a recent study of an industrial propylene/propane column (Finco et al., 1987). The column featured very long time constants and moderate nonlinearity. A number of different transfer function models were required in order to evaluate alternative choices of manipulated variables ( $R-V$ ,  $D-V$ ,  $RR-V$ , etc.). Because of the very long time constants, it took an excessive amount of computer time to try different size pulses for all configurations. In addition, the controller settings calculated from the resulting transfer functions

did not work well in many cases. This indicated that the transfer functions were not representing the column very accurately.

After some months of trying various methods, we found that the step of determining the transfer functions could be bypassed. We went directly to a fairly quick and easy-to-use procedure for getting reasonable and consistent controller settings that gave reliable comparisons of the alternative control configurations.

A modification of the BLT method (Luyben, 1986) was used. BLT tuning starts with the Ziegler-Nichols setting for each loop and detunes all loops equally until some multivariable robustness measure is satisfied. Therefore, the first thing that is needed is the ultimate gain  $K_u$  and ultimate frequency  $\omega_u$  of each of the individual SISO loops. We obtained these experimentally on the rigorous model of the column. All loops (except levels) were put on manual. One controller was put on automatic, and its gain was increased until a small-magnitude sustained oscillation in that loop occurred, giving  $K_u$  and  $\omega_u$  for that loop. This was repeated for each loop. The Ziegler-Nichols settings ( $K_{ZN}$  and  $\tau_{ZN}$ ) were calculated from the  $K_u$ 's and  $\omega_u$ 's.

Then a detuning factor  $F$  was assumed (typically about 2). Each gain was reduced by  $F$ , and each reset time was increased by  $F$ .

$$K_c = K_{ZN}/F$$

$$\tau_I = \tau_{ZN}F$$

Since the process open-loop transfer functions were not known, multivariable robustness measures could not be calculated. So we simply observed the load response of the nonlinear system for different values of the detuning factor  $F$ . The final value of  $F$  selected gave fairly conservative closed-loop damping coefficients (greater than 0.3).

This procedure took less computer time than the pulse testing route, and the resulting control systems worked well. However, the procedure did not yield transfer functions, so further analyses of stability, robustness, and integrity were not possible.

### Proposed Procedure

The methods used on the  $C_3$  splitter have been extended and improved so that an approximate transfer function model of a distillation column can be fairly easily obtained. The procedure is summarized below. Each individual step is then discussed in more detail. A numerical example is given later in this paper.

**A. Summary of Procedure.** (1) The steady-state gains are obtained by using a steady-state rating program.

(2) Each of the loops is "autotuned". The initial parts of the time response curves are used to read off the deadtimes in all the elements of the plant transfer function matrix.

(3) The autotuning gives ultimate gains and frequencies for the diagonal elements. During each of these runs, the amplitudes and phase angles are recorded for all the off-diagonal elements in the appropriate column (corresponding to the manipulative variable being used).

(4) Simple first-, second-, or third-order approximate transfer functions are fitted to the known data at zero frequency and at the ultimate frequency.

**B. Steady-State Gains.** Step 1 uses the normal procedure for obtaining steady-state gains. A small change is made in the value of one input ( $\Delta m_j$ ), and the steady-state values of the output variables ( $\Delta x_i$ ) are calculated. The ratio of  $\Delta x_i$  to  $\Delta m_j$  is the steady-state gain ( $K_{ij}$ ) of the  $ij$ th element in the plant transfer function matrix.

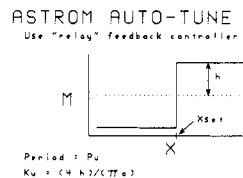


Figure 1. Relationship between controlled variable and manipulated variable using a relay in the feedback loop.

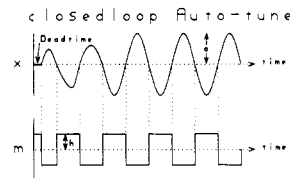


Figure 2. Illustration of autotune results.

Considerable caution should be taken to ensure that the convergence criteria in all parts of the steady-state program are very tight (sometimes down to  $10^{-10}$ ) and that very small changes are made in  $\Delta m$ 's. In the high-purity column discussed later, changes on the order of  $10^{-7}\%$  were required! Double-precision calculations are recommended for most computers.

**C. Autotune.** Step 2 is the autotuning procedure suggested by Astrom and Hagglund (1983). It is illustrated in Figures 1 and 2. A relay of height " $h$ " is inserted as a feedback controller. The manipulated variable  $m_j$  is increased by  $h$  above the steady-state value. When the controlled variable  $x_i$  crosses the set point, the relay reduces  $m_j$  to a value  $h$  below the steady-state value. The system will respond to this "bang-bang" control by producing a limit cycle, provided the system phase angle drops below  $-180^\circ$ , which is true for all real processes.

The period of the limit cycle is the ultimate period ( $P_u$ ) of the corresponding plant transfer function (the  $ii$ th diagonal element in the plant transfer function matrix). So the ultimate frequency is

$$\omega_u = (2\pi)/P_u \quad (1)$$

The ultimate gain of the same transfer function is given by

$$K_u = (4h)/(a\pi) \quad (2)$$

where  $h$  = height of the relay and  $a$  = amplitude of the primary harmonic of the output  $x_i$ .

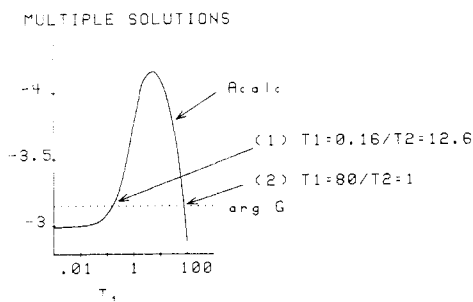
The amplitudes and phase angles of all the other outputs are also obtained for this periodically changing input  $m_j$ . This gives absolute magnitudes (magnitude ratios,  $|G|$ ) and arguments (phase angles,  $\arg G$ ) of all the other off-diagonal transfer functions in the same row of the plant transfer function matrix at this frequency.

The deadtime is read directly off the initial part of the time response curve for each output. This is illustrated in Figure 2.

Astrom's autotune method has several distinct advantages over open-loop pulse testing.

(1) No a priori knowledge of the system time constants is needed. The method automatically results in a sustained oscillation at the critical frequency of the process. The only parameter that has to be specified is the height of the relay step. This would typically be set at 1–5% of the manipulated variable range.

(2) It is a closed-loop test, so the process will not drift away from the set point. This keeps the process in the linear region where we are trying to get transfer functions. This is precisely why the method works on highly nonlinear



**Figure 3.** Illustration of multiple solutions for two-constant approximate transfer function.

processes. The process never is pushed very far away from the steady-state conditions.

(3) Very accurate information is obtained around the important frequencies, i.e., near phase angles of  $-180^\circ$ . In contrast, pulse testing tries to extract information for a range of frequencies. It therefore is inherently less accurate than a method which concentrates on a specific frequency range. This is particularly true for noisy signals. The higher and lower frequency noise can be filtered out, giving quite accurate data at one frequency. Remember, however, that we do not have to specify the frequency. The relay feedback automatically finds it.

Note that only  $N$  tests are required in an  $N \times N$  multivariable process, not  $N$  times  $N$  tests!

### Approximate Transfer Functions

The structure of the open-loop process transfer function matrix is

$$\begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_N \end{bmatrix} = \begin{bmatrix} G_{11} & G_{12} & \cdots & G_{1N} \\ G_{21} & \cdot & \cdot & \cdot \\ \vdots & \vdots & \ddots & \vdots \\ G_{N1} & \cdot & \cdot & G_{NN} \end{bmatrix} \begin{bmatrix} m_1 \\ m_2 \\ \vdots \\ m_N \end{bmatrix} \quad (3)$$

where  $x_i$  = controlled variable (output),  $m_j$  = manipulated variable (input), and  $G_{ij}$  = open-loop process transfer function relating  $x_i$  to  $m_j$ .

Step 3 yields values of absolute magnitudes and arguments of the complex numbers representing each of the  $N \times N$  transfer functions at a known frequency. For the diagonal elements, the argument is  $-180^\circ$  and the magnitude is the reciprocal of the ultimate gain  $K_u$ , which is calculated from eq 1:

$$\arg G_{ii} = -\pi \quad (4)$$

$$|G_{ii}| = 1/K_u \quad (5)$$

For the off-diagonal elements, arguments and magnitudes at a known frequency have been obtained in step 2. The zero-frequency magnitudes are also known (the steady-state gains).

Most distillation columns can be very adequately modeled by using simple first- and second-order transfer functions with deadtime and steady-state gain. Therefore, we assume that the transfer functions must be of one of the forms given below:

$$G_{ij} = \frac{K_{ij}e^{-D_{ij}s}}{(\tau_{ij}s + 1)^n} \quad n = 1, 2, \text{ or } 3 \quad (6)$$

$$G_{ij} = \frac{K_{ij}e^{-D_{ij}s}}{(\tau_{1ij}s + 1)(\tau_{2ij}s + 1)^n} \quad n = 1 \text{ or } 2 \quad (7)$$

where  $\tau$ ,  $\tau_1$ , and  $\tau_2$  are unknown time constants.

The best model and the power " $n$ " will be determined by selecting the form that best satisfies the equations given below:

model 1 (first-order lag):

$$\tau = (1/\omega)[(K/M)^2 - 1]^{1/2} \quad (8)$$

$$\tau = (1/\omega) \tan (A - \omega D) \quad (9)$$

model 2 (two equal first-order lags):

$$\tau = (1/\omega)[(K/M) - 1]^{1/2} \quad (10)$$

$$\tau = (1/\omega) \tan [(A - \omega D)/2] \quad (11)$$

model 3 (three equal first-order lags):

$$\tau = (1/\omega)[(K/M)^{1.5} - 1]^{1/2} \quad (12)$$

$$\tau = (1/\omega) \tan [(A - \omega D)/3] \quad (13)$$

model 4 (two unequal first-order lags):

$$M = \frac{K}{[1 + (\omega\tau_1)^2]^{1/2}[1 + (\omega\tau_2)^2]^{1/2}} \quad (14)$$

$$A = -\omega D + \arctan (-\omega\tau_1) + \arctan (-\omega\tau_2) \quad (15)$$

model 5 (one first-order and two equal first-order lags):

$$M = \frac{K}{[1 + (\omega\tau_1)^2]^{1/2}[1 + (\omega\tau_2)^2]} \quad (16)$$

$$A = -\omega D + \arctan (-\omega\tau_1) + 2 \arctan (-\omega\tau_2) \quad (17)$$

where  $M$  = magnitude of  $G$  and  $A$  = argument of  $G$ .

The equations above are applied sequentially to each of the transfer functions in the plant transfer function matrix. For each transfer function, the parameters that are known are  $K$ ,  $D$ ,  $M$ ,  $A$ , and  $\omega$ . The unknowns are the time constants: either the two  $\tau$ 's in pairs of eq 8/9, 10/11, and 12/13 or the two time constants  $\tau_1$  and  $\tau_2$  in eq 14/15 and 16/17.

To see if model 1 fits the data, eq 8 and 9 are solved for their  $\tau$  values. If the two values are approximately the same, it means that model 1 fits the data well. Similarly model 2 is tested by using eq 10 and 11 and model 3 with eq 12 and 13. The lowest order model that fits the data should be used. Note that if the deadtime in the model is zero, a third-order model must be used. The phase angle must drop below  $-180^\circ$  as frequency increases.

The evaluation of models 4 and 5 is a little more involved. The two equations for each model must be solved simultaneously for  $\tau_1$  and  $\tau_2$ . Sometimes there is no physical solution. For model 5, quite interestingly, sometimes there are two solutions!

The solution technique used was to guess a value for  $\tau_1$ . Then eq 14 or 16 was solved for  $\tau_2$ . Finally, the right-hand side of eq 15 or 17 was calculated; let us call this  $A_{\text{calc}}$ . If the actual argument of  $G$ ,  $A$ , was equal to  $A_{\text{calc}}$ , the correct values of  $\tau_1$  and  $\tau_2$  had been found.

Figure 3 illustrates a case where model 5 yielded two solutions: (a)  $\tau_1 = 0.16$ ,  $\tau_2 = 12.6$ ; (b)  $\tau_1 = 80$ ,  $\tau_2 = 1$ . The values of parameters that yielded these two solutions were  $K = 45.41$ ,  $D = 0$ ,  $M = 0.281$ ,  $A = \pi$ , and  $\omega = 1$ . Figure 4 compares the Bode plots of the two transfer functions: curve 1 is time-constant set a, and curve 2 is for set b. Note that they both pass through the same zero frequency and ultimate frequency points (when the phase angle is  $-180^\circ$ ).

### Example

The method was first tested on some simple known processes and worked well. Then some typical distillation

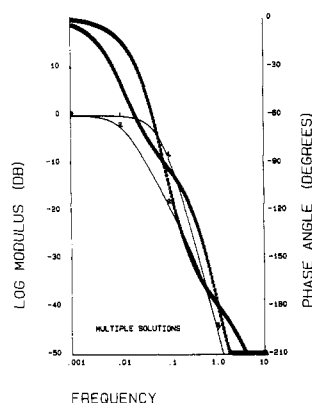


Figure 4. Bode plots of two transfer functions.

Table I. Design Parameters for 10 ppm Column

| compositions, mole fraction light |  |
|-----------------------------------|--|
| component                         |  |
| distillate, $x_D$                 | 0.99999  |
| bottoms, $x_B$                    | 0.00001  |
| feed, $z$                         | 0.50   |
| flow rates, kg-mol/min            |  |
| feed, $F$                         | 61.7   |
| distillate, $D$                   | 30.85  |
| bottoms, $B$                      | 30.85  |
| reflux, $R$                       | 21.579 248                                       |
| vapor, $V$                        | 52.429 248                                       |
| relative volatility               | 4  |
| trays                             |  |
| total, $N_T$                      | 40   |
| feed, $N_F$                       | 16 from bottom                                   |
| holdups, kg-mol                   |  |
| base                              | 466 (5 min)                                      |
| each tray in stripping section    | 28.04 (1-in. weir; height over weir = 1.487 in.) |
| each tray in rectifying section   | 19.75 (1 in. weir; height over weir = 0.604 in.) |
| reflux drum                       | 466 (5 min)                                      |
| transmitter spans                 |  |
| compositions, ppm                 | 50   |
| flows                             | twice steady-state flow rate                     |
| tray hydraulic time constant, min | 0.144  |

columns were used. Purity levels were 95–99%. Both ideal (constant relative volatility and equimolar overflow) and nonideal (methanol/water) binary systems were studied, as well as the ternary BTX system. Results were excellent. The transfer functions derived from the proposed method matched well with those obtained from pulse testing. Values for controller tuning constants worked very well on nonlinear simulations.

As a much more difficult test, the very high (10 ppm) purity column explored by Fuentes and Luyben (1983) was studied. This system is simple enough that analytical linearization can be used to get precise transfer functions. These were compared with the results of the proposed method.

Table I gives steady-state design parameters for the column. Assumptions were constant relative volatility, theoretical trays, total condenser, partial reboiler, equimolar overflow, saturated liquid feed and reflux, and perfect level controllers (constant levels in the base and reflux drum). A 5-min analyzer deadtime was used in both the  $x_D$  and  $x_B$  loops.

Table II compares the values of steady-state gains that were obtained from a rating program with those obtained from the analytical linearization (called LINDIS). The agreement is excellent, but extremely small changes ( $10^{-7}$ ) in the inputs had to be made. The process gains are reported in dimensionless form, using the values of flow and

Table II. Comparison of Dimensionless Steady-State Gains Obtained from Rating and Analytical Linearization (LINDIS)

|                  | LINDIS  | rating  |
|------------------|---------|---------|
| $K_{11} = x_D/R$ | 7 510   | 7 500   |
| $K_{12} = x_D/V$ | -18 250 | -18 100 |
| $K_{21} = x_B/R$ | 20 460  | 20 500  |
| $K_{22} = x_B/V$ | -49 910 | -49 800 |

Table III. Comparison of LINDIS and ATV

|                              | LINDIS    | ATV          |
|------------------------------|-----------|--------------|
| time constants               |           |              |
| $\tau_{11}$                  | 52 400    | 61 600       |
| $\tau_{12}$                  | 52 400    | 129 000      |
| $\tau_{21}$                  | 52 400    | 56 000       |
| $\tau_{22}$                  | 52 400    | 38 300       |
| ultimate gains ( $K_D/K_B$ ) | 1.67/0.22 | 1.66/0.20    |
| ultimate frequencies         | 0.16/0.23 | 0.15/0.25    |
| controller settings          | empirical | BLT          |
| detuning factor              |           | 2.95         |
| gains                        | 0.52/0.1  | 0.255/0.0315 |
| reset times, min             | 20/16     | 102/60.7     |

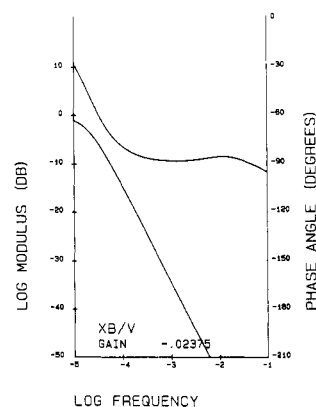


Figure 5. Bode plot for 10 ppm column.

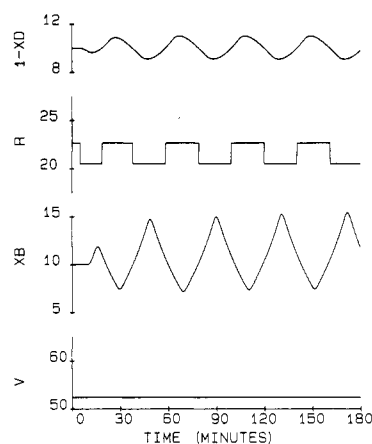


Figure 6. ATV test for 10 ppm column.

composition transmitter spans given in Table I. Note the very large process gains. This is a result of the very high purities. The controller gains reported later will have reasonable values, despite the large process gains, because of the attenuation that the very large time constants produce at frequencies near the closed-loop resonant frequency.

Figure 5 shows the Bode plot for  $G_{22}$  obtained from the analytically linearized model. The deadtime is not included in this plot. Note the extremely large time constant: 50 000 min! Note also that the system is essentially first order out to frequencies around 0.1 rad/min.

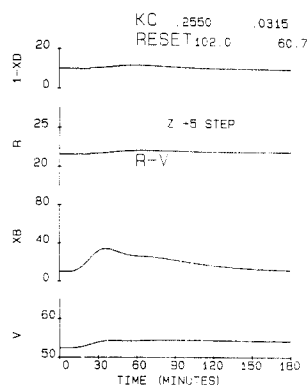


Figure 7. Feed composition disturbance with BLT controller settings derived from ATV transfer functions.

Figure 6 gives one of the autotune responses:  $x_D$  controlled by  $R$ . The height of the reflux relay was 5% of the steady-state value of reflux flow rate. Note that the responses are not pure sine waves. This is due to the non-linearity.

Table III gives the time constants, ultimate gains, ultimate frequencies, and controller settings (gain and reset times) from the proposed method (called "ATV") and from the analytically linearized model (called LINDIS). The agreement in ultimate frequency and ultimate gain is excellent, despite the fact that one of the time constants ( $\tau_{12}$ ) differs by a factor of 2. In the other, less nonlinear columns studied, the agreement between time constants obtained from pulse testing and ATV was quite good (within 10%). The 10 ppm column studied here is a very severe case, particularly since it exhibits one extremely large time constant that is 3 orders of magnitude away from the closed-loop resonant frequency.

Figure 7 gives the closed-loop response of the 10 ppm column for a step change in feed composition from 0.50 to 0.525. Analyzer deadtimes of 5 min were used in both the  $x_D/R$  and  $x_B/V$ . As discussed by Fuentes and Luyben (1983), this is a very difficult control problem. The BLT settings obtained from the transfer functions generated by the proposed ATV method were used in the controller on the nonlinear simulation. Stable dual-composition control was achieved. Responses to other moderately sized disturbances were similar, but very large disturbances threw the column into a very nonlinear region where the linear controllers could not cope.

Figure 8 gives the response of the column when the empirical controller settings recommended by Fuentes (1980) were used. These settings are very much tighter than those derived from BLT. The response using BLT settings is more stable.

**Extensions and Limitations.** The method has been tested on simulation studies of several columns. Additional evaluation on multicomponent, high-purity systems of complex configurations of columns is under way.

The use of more complex transfer functions than simple first-order lags will also be explored. Data at other frequencies would have to be obtained if more parameters are added to the model. One could visualize performing the autotuning first, getting the ultimate frequencies. Then more data could be obtained by direct sine-wave testing with each of the  $m_i$ 's at a frequency that was about half the ultimate frequency.

The proposed procedure has been developed and evaluated for distillation applications because of my interests. Its use in many other chemical engineering processes should be possible. It may even be usable in an operating plant environment.

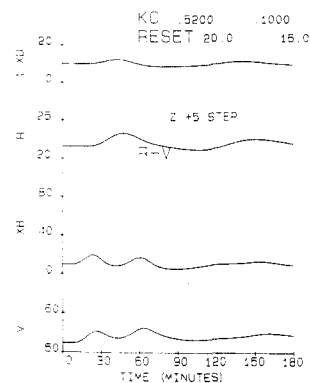


Figure 8. Feed composition disturbance with controller settings used by Fuentes (1980).

This procedure might be used on an open-loop unstable system in a single-loop process. However, in a multiloop process, the procedure appears to be limited to open-loop stable systems since only one loop is on automatic.

## Conclusions

A simple but effective method (ATV) has been developed to determine suitable transfer function models for highly nonlinear multivariable systems. The autotune method of Astrom is used to generate periodic data that are fitted to simple transfer functions. Evaluations of ATV on several distillation systems have produced very positive and useful results. The most severe case tested so far was a 10 ppm column. The ATV method handled this highly nonlinear column effectively.

## Acknowledgment

Thomas Rottner and S. M. Ding did the evaluations of the method on the moderate-purity methanol/water and ternary BTX systems.

## Nomenclature

- $A$  = argument of  $G$
- $a$  = amplitude of sine wave
- $A_{calc}$  = calculated  $\arg G$
- $\arg G$  = argument of  $G$  or phase angle of  $G$  (also called  $A$ )
- $D$  = deadtime, min
- $F$  = detuning factor or feed flow rate, kg-mol/min
- $G$  = open-loop plant transfer function
- $|G|$  = magnitude of  $G$  (also called  $M$ )
- $h$  = height of relay output change
- $K$  = steady-state gain of  $G$  ( $G_{(0)}$ )
- $K_c$  = controller gain
- $K_D$  = gain in  $x_D$  to  $R$  loop
- $K_B$  = gain in  $x_B$  to  $V$  loop
- $K_u$  = ultimate gain
- $K_{ZN}$  = Ziegler-Nichols gain
- $M$  = magnitude of  $G$
- $N$  = order of multivariable system (number of control loops)
- $P_u$  = ultimate period
- $R$  = reflux flow rate, kg-mol/min
- $s$  = Laplace transform variable
- $V$  = vapor boilup, kg-mol/min
- $x_B$  = bottoms composition, mole fraction light
- $x_D$  = distillate composition, mole fraction light
- $z$  = feed composition, mole fraction light

## Greek Symbols

- $\omega$  = frequency, rad/min
- $\tau$  = time constant, min
- $\tau_I$  = controller reset time, min
- $\tau_{ZN}$  = Ziegler-Nichols reset time, min

## Acronyms

ATV = autotune variation

BLT = biggest log-modulus tuning  
 LINDIS = linearized distillation  
 SISO = single input, single output  
 VLE = vapor-liquid equilibrium

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Received for review January 30, 1987

Revised manuscript received August 3, 1987

Accepted September 1, 1987

## Coreactant Hydroxyalkyl Phosphate Catalysts for Hydroxymelamine High-Solids Coatings

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A mixture of hydroxyalkyl phosphates has been prepared by the reaction of phosphorus pentoxide with 2-ethyl-1,3-hexanediol. These acid phosphates react with epoxy resins and simultaneously catalyze the hydroxymelamine condensation in aminoplast high-solids coatings. Similarly acrylic polymers with epoxy and hydroxy pendant groups can be reacted, in the presence of alkylated melamine resins, with these hydroxy phosphates to obtain high-solids coatings. In these compositions, the hydroxy phosphates act as coreactant catalysts and provide chain extension, cross-linking, and cure catalysis during baking. The preparation and use of hydroxyalkyl phosphates in the development of hydroxyepoxymelamine high-solids coatings has been described. The properties and accelerated weathering of the coatings have also been described.

Polyesters, acrylic polymers, and aminoplast resins comprise the major resin components in automotive topcoats and primers. Replacement of a  $\text{CH}(\text{CH}_3)$  by  $\text{P}(\text{CH}_3)$  or  $(\text{CH}_3)_2\text{P}(\text{O})$  in these acrylics and polyesters does not change the general physical properties; however, flammability is significantly reduced (Sander and Steininger, 1967). In addition to increased polarity and nonflammability, special effects can be assigned to the various organophosphorus functional groups. For example, incorporation of organophosphorus esters ( $\text{P}-\text{O}-\text{alkyl}$ ,  $\text{P}-\text{O}-\text{aryl}$ ), both in the main chain of the polymers and in the pendant groups, leads to pronounced internal plasticization, which is accompanied by lower softening temperature, an increase in impact strength, and a higher elongation at rupture. In addition to some of these desirable properties, organophosphorus esters have been reported to be antioxidants (Humphris and Scott, 1973) and adhesion promoters (Cassidy and Yager, 1971; Johnson et al., 1985). We have previously described the use of organophosphates in high-solids urethane coatings (Chattha, 1980a) and the use of alkyl acid phosphates in the development of hydroxymelamine high-solids coatings (Chattha, 1980b; Chattha and van Oene, 1982). In this paper we describe the preparation and use of alkyl acid phosphates bearing pendant hydroxides on the alkyl groups, to achieve additional cross-linking, in the development of hydroxymelamine high-solids coatings.

### Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer, and the molecular weight of the polymers was determined by gel permeation chromatography using propylene glycol P2000 (Waters Associates, Inc.) as a standard. The coatings were sprayed with a suction gun and baked in an air flow oven. The weathering of the coatings was examined on Q-Panel Company's QUV

cyclic weathering tester employing cycles of 8 h of light at 60 °C, followed by 4 h of darkness at condensing humidity at 50 °C. Other coatings evaluations and properties are listed in Table III.

**Materials.** Butyl methacrylate (BMA), ethylhexyl acrylate (EHA), glycidyl methacrylate (GMA), hydroxyethyl acrylate (HEA), hydroxypropyl methacrylate (HPMA), methyl methacrylate (MMA), and styrene were used without inhibitor removal in the synthesis of the polymers. Reagent-grade 2-ethyl-1,3-hexanediol and phosphorus pentoxide were used in the preparation of the hydroxyalkyl phosphates. Industrial-grade low viscosity aliphatic epoxy resin (Araldite CY178), bis(4,5-epoxy-2-methylcyclohexylmethyl) adipate, was obtained from Ciba-Geigy Corporation and was used without further purification. (Hexamethoxymethyl)melamine (Cymel 301) was obtained from American Cyanamid and was used as received. Technical-grade butyl acetate, methyl amyl ketone, and toluene were employed as solvents.

**Preparation of Hydroxyalkyl Phosphates.** Five hundred grams of dry 2-ethyl-1,3-hexanediol was placed under nitrogen in a three-necked flask fitted with a stirrer and a thermometer. Phosphorus pentoxide was added portionwise with continuous stirring. The addition of phosphorus pentoxide was regulated to maintain the temperature due to the exothermic reaction at 50 °C. Test portions of the reaction mixture were withdrawn at short intervals of time and titrated with KOH solution using phenolphthalein as indicator. The addition of phosphorus pentoxide was continued until the acid equivalent reached 280. The reaction mixture was stirred at 50 °C for one more hour and then filtered; its acid equivalent weight was 271.

**Preparation of Acrylic Polymers.** Acrylic polymers A, B, and C were prepared by conventional free-radical polymerization of vinyl monomers in toluene or methyl