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Experimental Evaluation of Analytical and Smith Predictors for Distillation Column Control

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Two time delay compensation techniques, the Smith predictor and the analytical predictor, are used for bottom composition control of a pilot scale methanol-water distillation column. The closed-loop performance of the two predictor schemes is compared to that for a proportional-integral controller in experimental and simulation studies. The predictors resulted in improved control for both set point and feed flow disturbances.

SCOPE

Significant time delays can occur in processes due to the presence of recycle loops, distance-velocity lags in fluid flow, and the dead time inherent in many composition analyses. The detrimental effects of time delays on closed-loop stability and control system performance are widely recognized. Thus, there is considerable motivation for the development of time delay compensation techniques that provide improved control of systems with significant time delays.

This investigation provides an experimental evaluation of two time delay compensation techniques, the Smith predictor (Smith, 1957, 1959) and the analytical predictor

(Moore, 1969; Moore et al., 1970). Both techniques employ a simple dynamic model to predict future outputs based on current information. These time delay compensation techniques and a conventional proportional-integral (PI) controller are used to control the bottom composition of a pilot scale, methanol-water, distillation column. The same techniques have been evaluated for top composition control in a related study (Meyer et al., 1977).

This investigation and the related study (Meyer et al., 1977) provide the first experimental applications of time delay compensation techniques to distillation column control that have been reported in the open literature.

CONCLUSIONS AND SIGNIFICANCE

In general, the analytical and Smith predictor control schemes performed better than a PI controller in controlling the bottom composition of the pilot scale column. The

simulation study demonstrated that both time delay compensation techniques can provide significant improvements in regulatory and servo control. Use of the analytical predictor resulted in shorter settling times and lower integral absolute error (IAE) values than the Smith predictor, which, in turn, outperformed the PI controller. The experimental results tended to support the conclusions from the simulation study, but the degree of improvement that

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was obtained using the analytical and Smith predictors was less significant. The relatively poor performance of the predictors in the experimental study is attributed to the presence of a large time delay, associated with the sample loop, that was not included in the predictor model. By contrast, for top composition control of the same column, where there was no such modeling error, the predictor control schemes provided substantial improvements in both simulation and experimental studies (Meyer et al., 1977).

It is encouraging that in this application improved control was obtained using simple transfer function process models, since such models are often available, or can be easily obtained, in industrial applications. The analytical and Smith predictor control schemes are recommended for distillation control problems where adequate quality control cannot be obtained via temperature regulation and where long time delays exist in composition control loops.

THEORETICAL DEVELOPMENT

Improved control of distillation columns is an important topic owing to the widespread use of distillation columns in the process industries and their large energy requirements. The continuing interest in distillation control strategies is exemplified by the recent books by Shinskey (1977) and Rademaker et al. (1975). Tight composition control of industrial columns is often difficult owing to the presence of long time delays for composition analysis. These time delays can range from 30 min to several hours if the composition analyzer is located on a downstream column rather than on the column of interest.

The block diagram representation of a process containing time delays and a conventional feedback control system is shown in Figure 1. The feedback controller transfer function $G_c(s)$ is to be designed so that the closed-loop system is stable, and the controlled variable C remains at or near the set point R_{set} . If time delays T_1 and T_2 are large, these design objectives may be difficult to achieve, since the controller gain must be reduced in order to ensure stability, but low controller gains also produce long response times.

Smith Predictor (SP)

Of the time delay compensation techniques that have been proposed, the Smith predictor (Smith, 1957, 1959) has received the most attention. Use of the Smith predictor (SP) can result in significant improvements over conventional PID control as has been demonstrated in experimental applications (Doss and Moore, 1973; Doss, 1974; Buckley, 1960; Lupfer and Oglesby, 1961, 1962; Alevsakakis and Seborg, 1974; Prasad and Krishnaswamy, 1975) and simulation studies (Nielsen, 1969; Smith and Groves, 1973; Meyer et al., 1976). However, Nielsen (1969) and the authors (Meyer et al., 1976) have shown that such improvement does not always occur for regulatory control, even for the ideal case where a perfect process model is used in the predictor. The sensitivity of the SP method to modeling errors is an important practical consideration which has been considered in several studies (Buckley, 1960; Eisenberg, 1967; Garland and Marshall, 1974, 1975; Marshall, 1974). In recent years, the SP approach has been extended to sampled data systems (Doss and Moore, 1973; Marshall, 1974; Gray and Hunt, 1971a, b; Alevsakakis and Seborg, 1973) and multivariable control problems (Alevsakakis and Seborg, 1973, 1974; Mee, 1973).

A block diagram of the discrete form of the Smith predictor, including a zero-order hold (ZOH), is shown in Figure 2. In Figure 2 c_k , u_k , and d_k denote the values of variables C , U , and D , respectively, at the k^{th} sampling instant. The feedback loop around the digital controller contains a block whose output represents the difference

between the response of the system without time delays c_k' and the response of the system which contains time delays c_k'' . For the ideal case where the process model is exact, $c_k'' = c_k$, and from Figure 2 it follows that $e_k = r_k - c_k'$. Thus, the control action is based on c_k' , the response of the undelayed model, and time delays T_1 and T_2 do not appear in the characteristic equation. This means that a larger controller gain can be used, and the response time of the closed-loop system will be reduced. In practice, the presence of modeling errors will prevent some of this improvement from being realized.

In this application, the process model is considered to be a first-order system plus time delay:

$$\tau_p \frac{dc}{dt} + c(t) = K_p u(t - T) \quad (1)$$

where T is $T = T_1 + T_2$, or, equivalently, $T = (N + \beta)T_s$, where $0 \leq \beta < 1$. Since a digital controller and a zero-order hold are being used, the manipulated variable remains constant between sampling instants. Integrating Equation (1) over the time interval between the $(k - 1)$ and k^{th} sampling instants and denoting the model response by c_k'' , we get (Meyer, 1977)

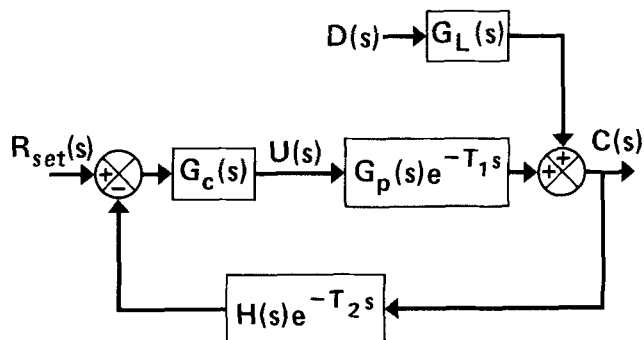


Fig. 1. Conventional feedback control system.

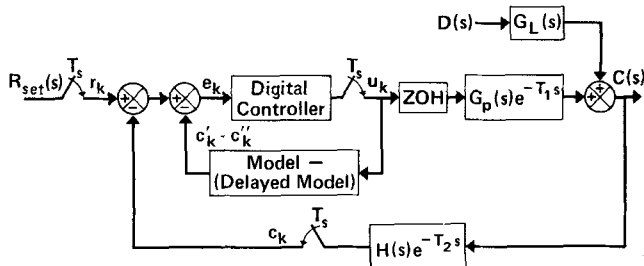


Fig. 2. Smith predictor (SP) control system.

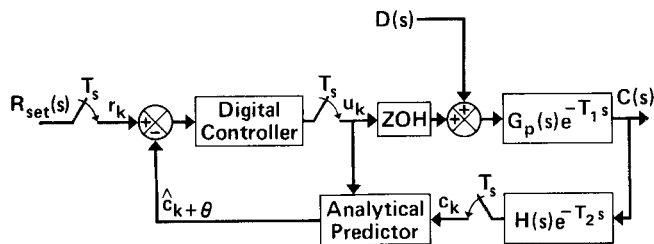


Fig. 3. Analytical predictor (AP) control system.

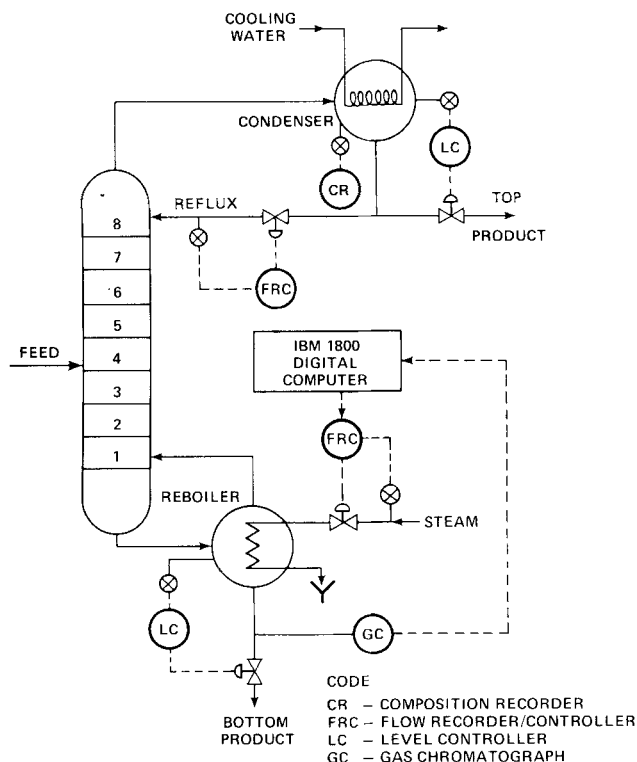


Fig. 4. Schematic diagram of the distillation column.

$$c''_k = B c''_{k-1} + B K_p \left(\frac{1}{E} - 1 \right) u_{k-N-2} + K_p \left(1 - \frac{B}{E} \right) u_{k-N-1} \quad (2)$$

where $B \triangleq \exp[-T_s/\tau_p]$ and $E \triangleq \exp[-\beta T_s/\tau_p]$. If no time delays are present (that is, $T = 0$), then the corresponding expression for the undelayed model is given by

$$c'_k = K_p(1 - B)u_{k-1} + B c'_{k-1} \quad (3)$$

From Figure 2, it follows that the error signal e_k can be expressed as

$$e_k = r_k - c_k - (c'_k - c''_k) \quad (4)$$

If a conventional PI digital control algorithm is employed, then

$$u_k = K_c \left[e_k + \frac{T_s}{\tau_I} \sum_{i=1}^k e_i \right] \quad (5)$$

Analytical Predictor (AP)

An alternative approach for time delay compensation in feedback control systems, the analytical predictor, has been developed by Moore (1969). In his approach, a

process model is used to predict the future output from current measurements, and the predicted value is then sent to the controller. Simulation studies by Moore (1969) and Moore et al. (1970) have shown that the analytical predictor can result in better performance than a PI controller and is quite insensitive to modeling errors. The AP method has been studied experimentally by application to control of a stirred-tank heating system (Doss and Moore, 1973) and top composition control of a distillation column (Meyer et al., 1977). In these investigations, both the AP and SP predictors performed better than a PI controller.

A block diagram illustrating the analytical predictor control scheme is shown in Figure 3, with $\hat{c}_{k+\theta}$ denoting the predicted output over a time interval θT_s , where

$$\theta = \frac{T}{T_s} + 0.5 = N + \beta + 0.5 \quad (6)$$

Thus, $\hat{c}_{k+\theta}$ is a prediction of the future output over a time interval of $(N + \beta + 0.5)T_s$, where $(N + \beta)T_s$ is the total system time delay, and $0.5T_s$ is a correction for the effect of sampling and the zero-order hold. This correction is somewhat redundant, since the derivation in Equations (1) to (4) implicitly takes into account sampling and the operation of the zero-order hold. However, the $0.5T_s$ correction may provide beneficial predictive action and thus will be retained. Moore et al. (1970) derived the following expression for $\hat{c}_{k+\theta}$ from the analytical solution of Equation (1):

$$\hat{c}_{k+\theta} = A \hat{c}_{k+N+\beta} + K_p(1 - A)u_k \quad (7)$$

where

$$\begin{aligned} \hat{c}_{k+N+\beta} = & EB^N c_k + B^N K_p(1 - E)u_{k-N-1} \\ & + K_p(1 - B) \sum_{i=1}^N B^{i-1} u_{k-i} \end{aligned} \quad (8)$$

and $A \triangleq \exp[-T_s/2\tau_p]$. The predicted output is then used in a proportional control algorithm of the form

$$u_k = K_c(\rho_k - \hat{c}_{k+\theta}) \quad (9)$$

where ρ_k is given by

$$\rho_k = \frac{K_c K_p + 1}{K_c K_p} r_k \quad (10)$$

Set point calibration is required to eliminate the offset (that is, steady state error) that occurs after step changes in set point when only proportional control is used.

Moore et al. (1969, 1970) have also proposed a second control algorithm to compensate for unknown disturbances which inevitably occur in process control systems. If the disturbance can be measured, then Equation (9) can be modified to give

$$u_k + d_k = K_c(\rho_k - \hat{c}_{k+\theta}) \quad (11)$$

Note that in Equation (11), d_k has been added to u_k because the block diagram in Figure 3 indicates that d_k and u_k affect c_k in the same manner. For the more usual situation where the disturbance cannot be measured, an estimated disturbance \hat{d}_k can be used in place of d_k to yield Equation (12):

$$u_k + \hat{d}_k = K_c(\rho_k - \hat{c}_{k+\theta}) \quad (12)$$

TABLE 1. TYPICAL OPERATING CONDITIONS

Feed flow rate, F	18 g/s
Reflux flow rate, R	16 g/s
Steam flow rate, S	14 g/s
Feed composition, C_F	50%
Top composition, C_D	97%
Bottom composition, C_B	5%
Distillate flow rate, D	8.8 g/s
Bottom flow rate, B	9.2 g/s

By assuming that the disturbance is a step input of unknown magnitude, Moore et al. (1969, 1970) derived the following expression for \hat{d}_k :

$$\hat{d}_k = \hat{d}_{k-1} + K_I T_s (c_k - \hat{c}_k) \quad (13)$$

where \hat{c}_k is the prediction made at time, $(k - \theta)T_s$. Although an expression for K_I can be derived in terms of B and E , K_I is generally used as a tuning parameter in the AP control scheme (Moore, 1969).

The estimated disturbance \hat{d}_k can also be incorporated into Equations (7) and (8) in order to provide a better prediction of the future output:

$$\hat{c}_{k+\theta} = A\hat{c}_{k+N+\beta} + K_p(1-A)(u_k + \hat{d}_k) \quad (14)$$

where

$$\begin{aligned} \hat{c}_{k+N+\beta} = & EB^N c_k + B^N K_p(1-E)(u_{k-N-1} + \hat{d}_k) \\ & + K_p(1-B) \sum_{i=1}^N B^{i-1}(u_{k-i} + \hat{d}_k) \end{aligned} \quad (15)$$

By combining Equations (12) to (15), the following expression for the AP control law is obtained:

$$u_k = \frac{K_c}{1 + K_c K_p(1-A)} (\rho_k - A\hat{c}_{k+N+\beta}) - \hat{d}_k \quad (16)$$

Note that the AP control algorithm in Equations (13), (15), and (16) contains several parameters which can be adjusted. In previous studies by Moore et al. (1969, 1970) and Doss and Moore (1973, 1974), K_c and K_I were considered to be control parameters which could be tuned on-line, while A , B , E , and K_p were considered to be constant model parameters. This same approach is adopted in the present investigation. It should also be noted that inclusion of the disturbance estimate \hat{d}_k in Equation (16) provides a form of integral action, since the estimated disturbance will change with time until $\hat{c}_k = c_k$ [see Equation (13)].

EQUIPMENT

Description

The experimental equipment consists of a methanol-water pilot scale distillation column interfaced with an IBM 1800 data acquisition and control computer. A schematic representation of the equipment and control scheme is shown in Figure 4. The 22.5 cm diameter column contains eight trays fitted with four bubble caps per tray and a tray spacing of 30.48 cm. The column is equipped with a total condenser and thermosyphon type of reboiler. Bottom composition is measured with an HP-5720A gas chromatograph (GC) under computer controlled sampling and analysis of the chromatogram. In-line liquid sampling on a 4 min cycle basis is employed. The control configura-

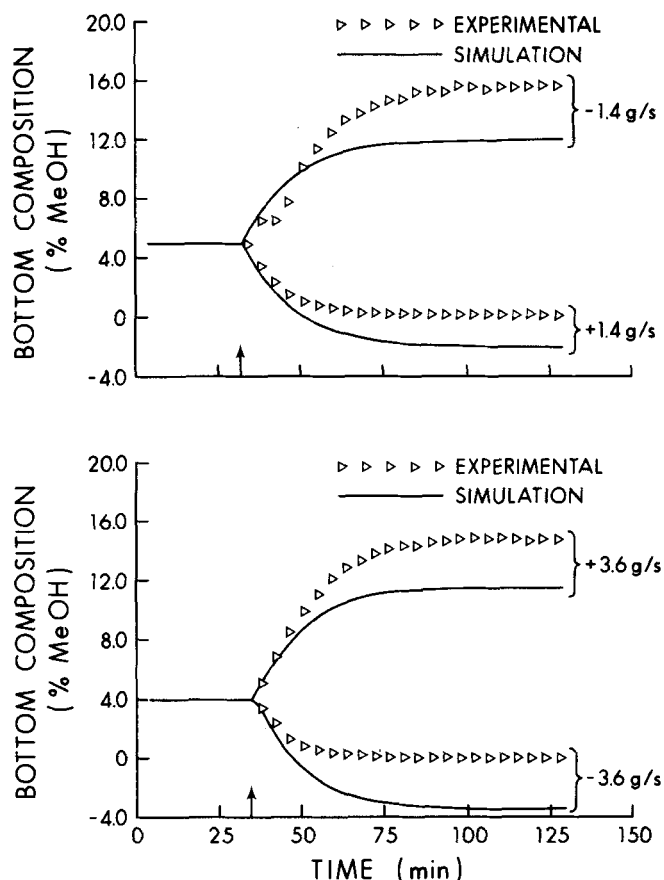


Fig. 5. Open-loop responses for step changes in steam (top) and feed flow (bottom).

tion involves the control of bottom composition by manipulation of steam flow rate. As can be seen from Figure 4, the system operates in an analogue supervisory mode in that the computer output, which is calculated using the composition results from the GC, is sent as a set point to the analogue steam flow controller. The distillation column is equipped with extensive instrumentation (Svreck, 1967; Pacey, 1973) which allows measurement of all temperatures, flows, and pressures as well as continuous top composition analysis. All variables are monitored/controlled using the standard direct digital control program of the IBM 1800.

Process Model

In order to employ either the Smith predictor or the analytical predictor control schemes, a mathematical model of the process must be available. Although the dynamics of the distillation column are inherently nonlinear, for operation near a nominal steady state the dynamics can be adequately approximated by a first order plus time delay transfer function model (Pacey, 1973; Wood and Berry, 1973). For the nominal operating conditions given in Table 1, an appropriate first order plus time delay transfer function model relating the effect of steam flow S and the feed flow rate F on bottom composition C_B is

$$C_B(s) = \frac{-5.0 e^{-2.9s}}{14.4s + 1} S(s) + \frac{2.08 e^{-3.4s}}{13.2s + 1} F(s)$$

Flow rates are expressed in grams per second and the composition in percent methanol. Time constants and time delays are expressed in minutes. It should be noted that these transfer functions do not include the measurement dynamics which are represented by an ideal sampler and a time delay of 4 min for the GC analysis.

TABLE 2. SIMULATION RESULTS: CONTROLLER PARAMETERS AND IAE VALUES

Control scheme	Controller parameters		IAE values (%s)	
	K_c (g/s/%)	τ_I (s)	+2% change in set point	-17% change in feed flow rate
PI	-0.256	1 167	1 970	5 700
SP	-0.696	574	1 136	3 630
AP	-1.34	-0.00343*	1 073	1 800

* K_I value expressed in units of (grams per second)/(percent)(seconds).

A comparison of simulated and experimental open-loop responses for step changes in steam and feed flow rate is shown in Figure 5. Obviously, the parameter values of the transfer function model represent a compromise, since the linear process model is only approximate owing to the inherent nonlinearity of the column. In particular, note that for a decrease in steam flow rate and in increase in feed flow rate, the simulated response is below the experimental response, suggesting that a higher process gain should be employed. However, comparison of the simulated and experimental responses for step changes in the opposite directions implies that the process gain should be decreased rather than increased. For these changes, the simulated response is physically unrealizable owing to negative compositions, which again demonstrates the limitations of the transfer function model.

SIMULATION RESULTS

Digital computer simulation using the IBM S/360 CSMP program was carried out to evaluate the performance of the Smith predictor and analytical predictor control schemes compared to PI control. The SP algorithm in Equations (2) to (5) and the AP algorithm in Equations (13) to (16) were employed with a sampling interval of 4 min ($T_s = 4$). Digital PI controller constants were calculated using a modification of the approach suggested by Moore et al. (1969). They proposed calculating the controller constants using the minimum integral of the absolute error (IAE) tuning relations for continuous controllers with the process time delay T replaced by an effective time delay $T' = T + T_s/2$. In the present study, control performance using controller constants calculated from the IAE tuning relations in Equations (17) and (18)

$$K_c = \frac{0.984}{K_p} \left(\frac{T'}{\tau_p} \right)^{-0.986} \quad (17)$$

$$\tau_I = 1.644 \tau_p \left(\frac{T'}{\tau_p} \right)^{0.707} \quad (18)$$

was not satisfactory. Instead, controller constants were calculated by considering the effective time delay to be $T' = T + T_s$, as suggested by Mollenkamp et al. (1973), and this resulted in satisfactory control. It is to be noted that this value of T' corresponds to the largest possible

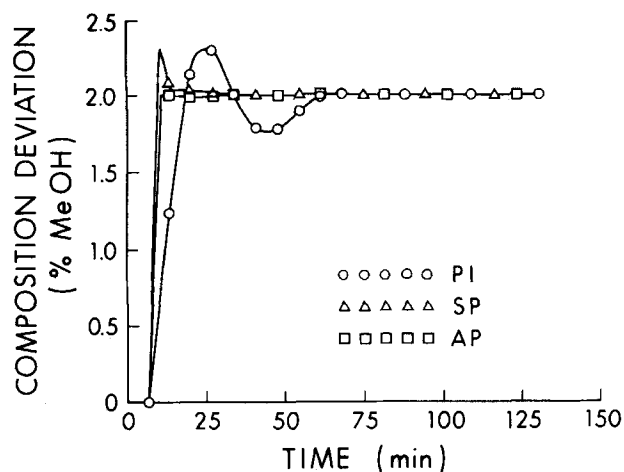


Fig. 6. Comparison of closed-loop responses for a 2% step increase in set point.

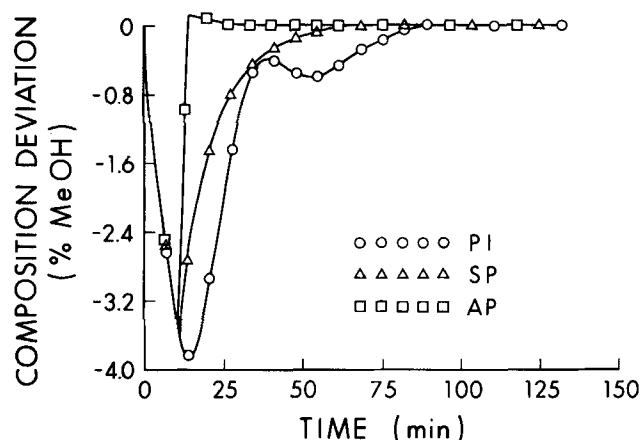


Fig. 7. Comparison of closed-loop responses for a 17% step decrease in feed flow rate.

time delay due to sampling (for example, a load disturbance occurring immediately after a sampling instant). Since the Smith predictor also contains a PI controller, in principle the same approach can be used. Satisfactory control was achieved using an effective time delay of $T' = T_s$ rather than $T' = T_s/2$. The process time delay was not included, since the Smith predictor itself compensates for this time delay. The controller constants for the analytical predictor were calculated using the deadbeat controller relations of Moore (1969) given in Equations (19) and (20):

$$K_c = \frac{A}{K_p(1-A)} \quad (19)$$

$$K_I = \frac{1}{T_s K_p(1-B)} \quad (20)$$

Typical simulated responses are shown in Figure 6 for a 2% step increase in set point and Figure 7 for a 17%

TABLE 3. CONTROLLER CONSTANTS FOR THE EXPERIMENTAL TESTS

Control technique	Simulation study			Experimental study		
	K_c , (g/s)/(%)	τ_I , s	K_I , (g/s)/(%) (s)	K_c , (g/s)/(%)	τ_I , s	K_I , (g/s)/(%) (s)
PI	-0.256	1 167	—	-0.15	1 500	—
SP	-0.696	574	—	-0.20	1 200	—
AP	-1.34	—	-0.00343	-0.20	—	-0.0020

step decrease in feed flow rate. A summary of controller constants and IAE values for the simulation is given in Table 2.

The IAE values in Table 2 and Figures 6 and 7 indicate that both predictor control schemes provide improvements compared to PI control. For set point changes, the PI controller exhibited a slow oscillation compared to the Smith predictor which produced a small overshoot and a short settling time. In contrast, the analytical predictor

moved the composition directly to the set point without overshoot. The results in Figure 7 demonstrate that the behavior of the different control schemes is similar for a feed flow disturbance, but the response times are markedly shorter for the analytical and Smith predictor control schemes than for PI control. It should be noted that attempts to tune the PI controller to reduce the IAE values were not successful.

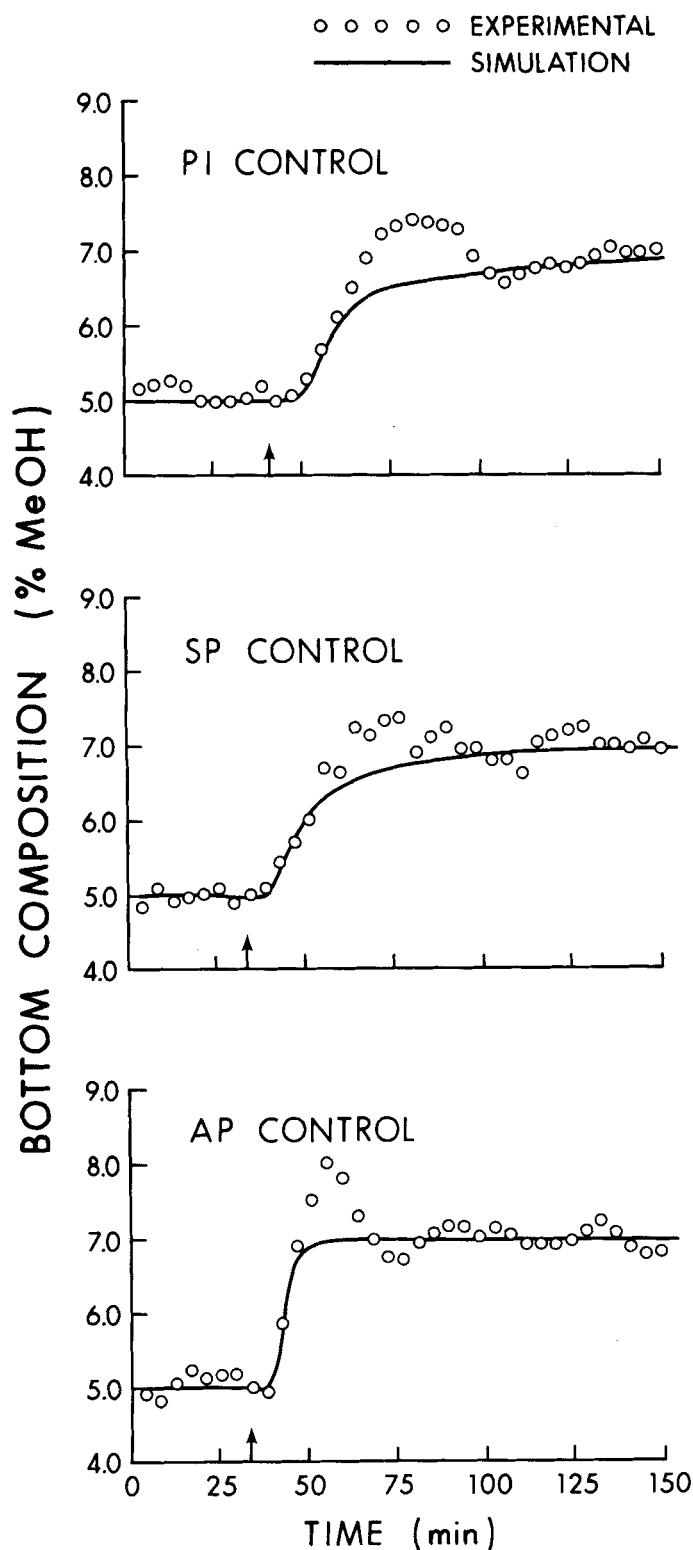


Fig. 8. Comparison of simulated and experimental closed-loop responses for a 2% step increase in set point.

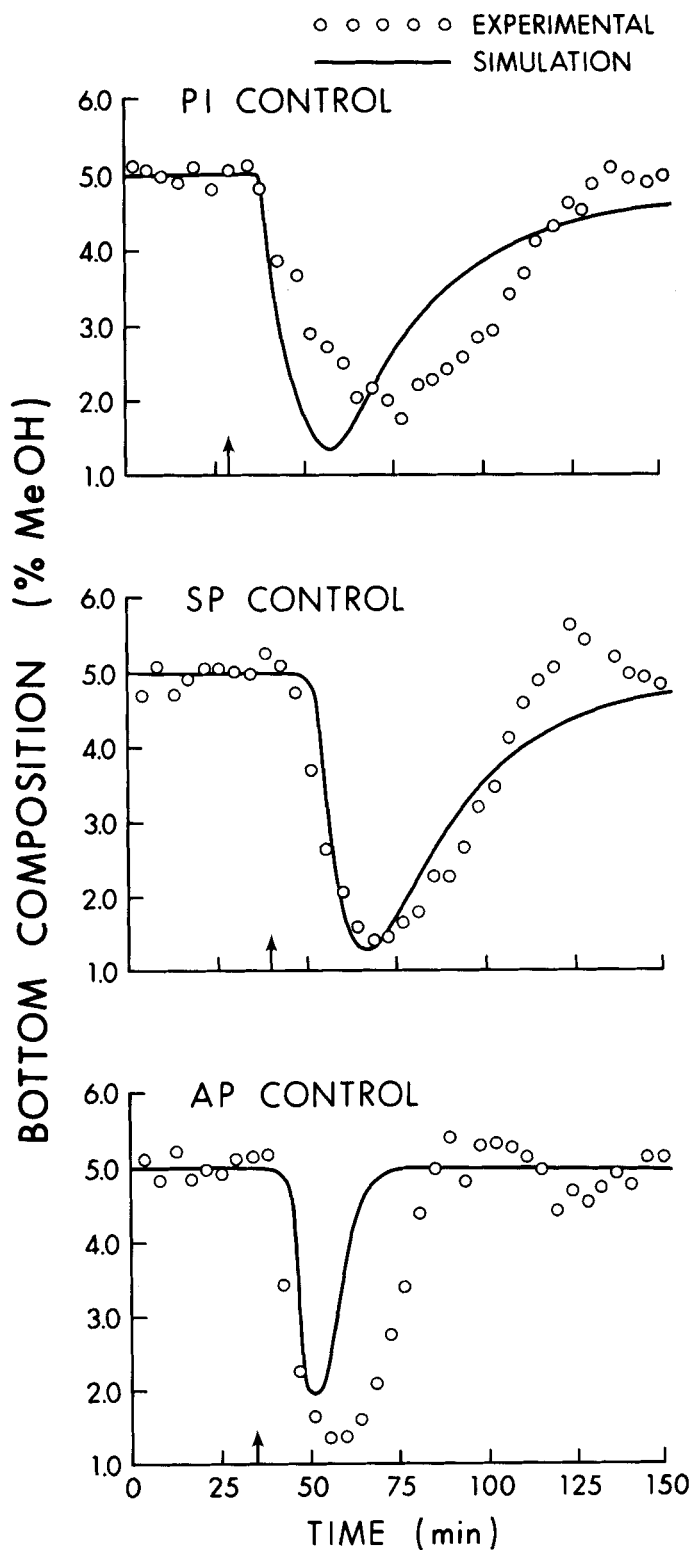


Fig. 9. Comparison of simulated and experimental closed-loop responses for a 17% step decrease in feed flow rate.

TABLE 4. EXPERIMENTAL RESULTS: COMPARISON OF IAE VALUES

Control scheme	Set point changes		Load changes	
	+2%	-2%	+17%	-17%
PI	3 250	3 850	10 000	10 400
SP	3 350	2 600	6 600	9 600
AP	2 500	2 200	7 200	7 400

EXPERIMENTAL RESULTS

Experimental tests on the pilot scale column were made using step changes of $\pm 2\%$ in set point and $\pm 17\%$ in feed flow rate. Since the calculated controlled constants in Table 2 produced experimental responses which were very oscillatory, on-line tuning of the controller param-

eters for each of the control schemes became necessary. The open-loop responses in Figure 5 indicate that the process gain is higher for set point or load changes which cause the composition to increase from the normal set point and that the gain is lower for changes which cause decreases from the set point. Consequently, the controller constants were tuned for an increase in composition set point which ensured that they were conservative for disturbances leading to a reduction in bottom composition. The IAE performance criterion was selected as the basis for tuning controller constants. A comparison of the calculated constants for the simulation study and those determined by on-line tuning is given in Table 3.

As can be seen in Table 3, it was necessary to use more conservative controller constants in order to obtain satisfactory control. Figures 8 and 9 show the experimental and simulated responses when the experimentally tuned

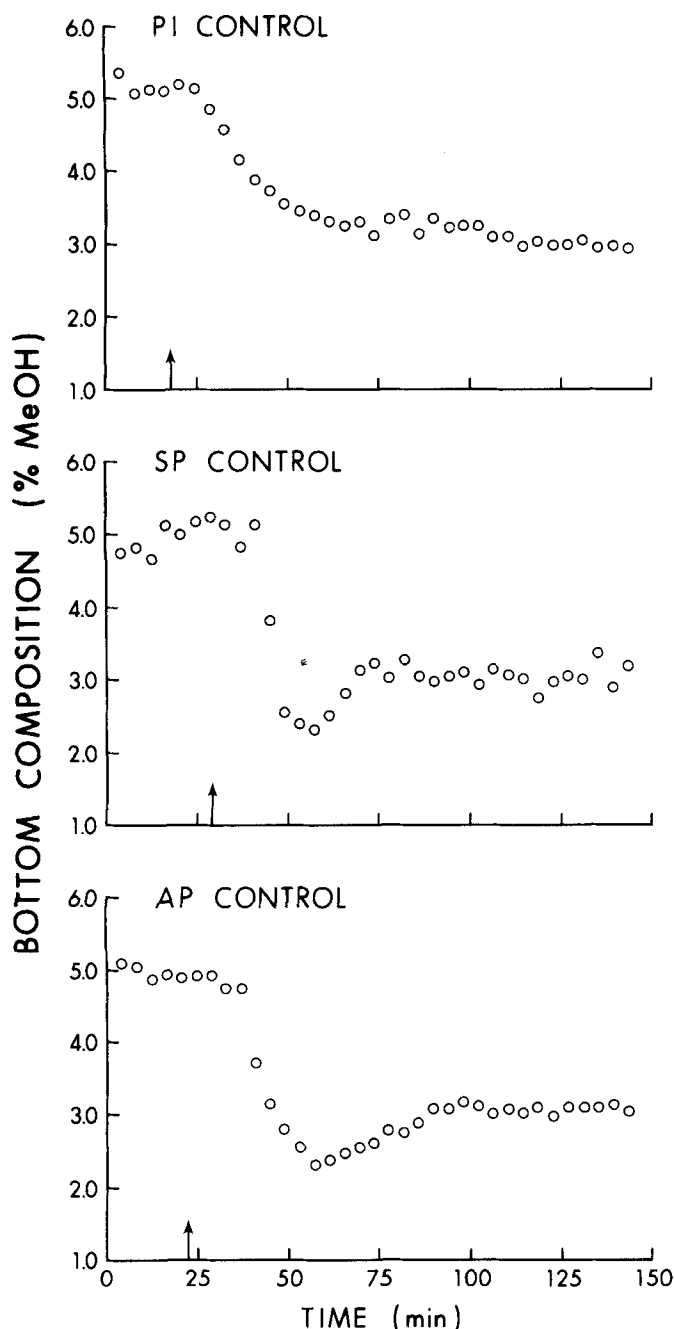


Fig. 10. Experimental comparison of PI, SP, and AP control for a 2% step decrease in composition set point.

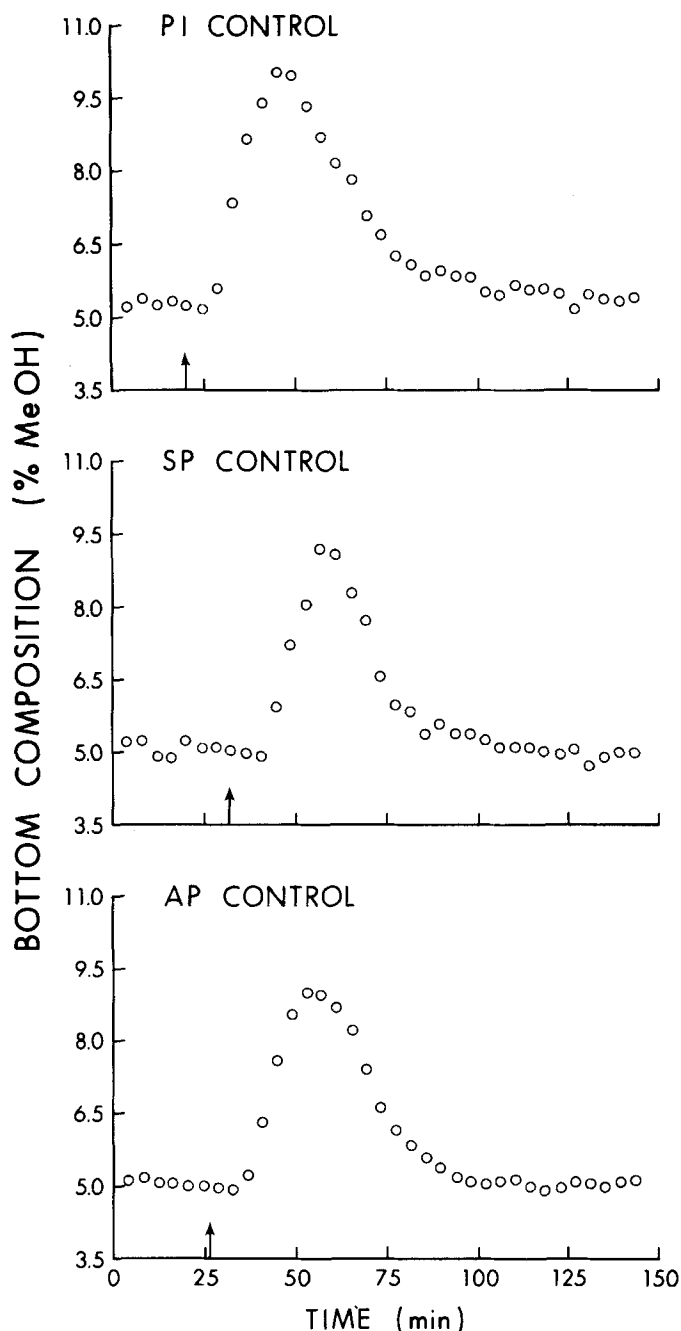


Fig. 11. Experimental comparison of PI, SP, and AP control for a 17% step increase in feed flow rate.

controller constants are employed. The IAE value for these experimental tests are given in Table 4.

Examination of the IAE values demonstrated the improved performance that can be achieved using a predictor control scheme. For the +2% set point change, the Smith predictor control system produced a slightly larger IAE value than the PI controller, whereas analytical predictor control was clearly superior. The simulated responses in Figures 8 and 9 indicate that the experimentally tuned controller constants exhibit very conservative control of the simulated process. This is in marked contrast to the simulation results in Figures 6 and 7, where the controller constants were based on the transfer function model. Consideration of the experimental response in Figure 8 suggests that had the controller constants been altered, the tendency to overshoot could have been eliminated. This is, in fact, the case, as discussed previously for the simulated responses, but the result would have been larger IAE values than those in Table 4. Likewise, the experimental control behavior shown in Figure 9 could have been altered to reduce the maximum deviation, but the result would be excessive oscillation about the set point leading to a larger IAE value.

The difficulty in selecting controller constants due to the inherent nonlinearity of the column is illustrated by the closed-loop responses shown in Figures 10 and 11. Here, the tuned controller constants in Table 3 were used to generate the closed-loop response to a 2% step decrease in set point and a 17% step increase in feed flow, respectively. For the decrease in set point, the PI response is overdamped in contrast to the underdamped response for the increase in set point shown in Figure 8. This trend is also apparent for the Smith and analytical predictor control schemes. A comparison of the results in Figures 9 and 11 indicates that for an increase in feed flow, the composition returns to the set point in a much shorter time than for the case of a decrease in feed flow rate.

After the experimental study had been completed, it was discovered (Tong, 1979) that a time delay of nearly 16 min existed in the bottom composition sample recirculation loop. This large time delay was inadvertently introduced during a recent equipment modification, when a fine porosity large bowl cartridge filter was installed in the sample recirculation loop. Consequently, in the experimental study, the SP and AP operated under a severe disadvantage, since the process model contained a gross modeling error (that is, a time delay of 2.9 min vs. an actual time delay of $2.9 + 16 = 18.9$ min). Despite this significant modeling error, the SP and AP methods performed somewhat better than the PI controller. If the actual time delay of 18.9 min had been included in the process model, it is very likely that the predictor methods would have provided significant improvements over PI control, as was observed in the simulation study.

The experimental results demonstrate that the controller constants for the SP and AP methods can be tuned on-line to partially compensate for modeling errors. These results are quite encouraging for industrial applications, where only approximate process models may be available.

ACKNOWLEDGMENT

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NOTATION

$A = \exp(-T_s/2\tau_p)$
 $AP =$ analytical predictor
 $B = \exp(-T_s/\tau_p)$

$C, c =$ output (controlled variable)
 $c' =$ output of system without time delay
 $c'' =$ output of system with time delay
 $C_B =$ bottom composition
 $C_D =$ top composition
 $C_F =$ feed composition
 $D =$ distillate flow rate (Table 1)
 $D, d =$ load disturbance
 $e =$ controller input
 $E = \exp(-\beta T_s/\tau_p)$
 $F =$ feed flow rate
 $G_c =$ controller transfer function
 $GC =$ gas chromatograph
 $G_L =$ load transfer function
 $G_p =$ process transfer function
 $H =$ measurement transfer function
 $IAE =$ integral absolute error
 $k =$ positive integer
 $K_c =$ controller gain
 $K_I =$ integral controller constant
 $K_p =$ process gain
 $N =$ nonnegative integer
 $PI =$ proportional-integral control
 $R =$ reflux flow rate
 $R_{set}, r =$ set point
 $S =$ steam flow rate
 $s =$ Laplace operator
 $SP =$ Smith predictor
 $T, T', T_1, T_2 =$ time delays
 $T_s =$ sampling period
 $U, u =$ manipulated variable
 $ZOH =$ zero-order hold

Greek Letters

$\beta =$ constant, $0 < \beta < 1$
 $\theta =$ dimensionless time delay
 $\rho =$ calibrated set point
 $\tau_I =$ reset time
 $\tau_p =$ process time constant

Subscript

$k =$ value at the k^{th} sampling instant

Superscript

$\wedge =$ predicted value

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An Experimental Study of the Rheological Behavior of Surface Films

A constitutive equation has been developed to relate surface stresses to the deformational history of an interface. To verify the applicability of the equation to real surface films, experimental studies involving spread and adsorbed monolayers have been conducted using the deep-channel surface rheometer operated both under the conditions of oscillatory and constant floor motion. The results reported here are the first obtained using an oscillatory system.

Experimental results indicate that both spread and adsorbed monolayers can exhibit viscoelastic behavior which may be represented by the model. Furthermore, it has been found that for three long chain, fatty acid films, spread on a pH 6.1 aqueous substrate, surface shear viscosity and surface elasticity increase with film pressure and molecular weight. The observed rheological behavior was found to be strongly pH dependent.

SCOPE

An interfacial constitutive equation has been proposed (Gardner et al., 1977) which allows for both non-Newtonian steady shear and viscoelastic behavior and thus provides a unified description of complex interfacial phenomena. The objective of this study is to verify the applicability of this constitutive equation and associated models to real surface films. In order to achieve this, rheological

experiments have been conducted with spread films of long chain, fatty acids and an adsorbed polymeric film using the deep-channel surface rheometer (Gardner et al., 1977; Burton and Mannheimer, 1967; Mannheimer and Schechter, 1970). In order to evaluate the parameters associated with the proposed constitutive equation, a new experimental technique which employs a small amplitude sinusoidal deformation has been used in conjunction with surface viscometry.

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