

Hydroquinone oxidation kinetics in adsorptive liquid chromatographic beds

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ABSTRACT

Catalytic properties of chromatographic silicas modified with ferric ions using a batch preparation process are compared with those modified *in situ* in a column on the basis of the hydroquinone oxidation to benzoquinone in a liquid chromatographic reactor. This is done through application of a statistical moment method for kinetic parameter estimation from reactor chromatograms. The first absolute moment of the overall elution profile is utilized to evaluate the pseudo-first order rate constants for oxidation both with and without consideration of hydroquinone sorption processes. In general, hydroquinone adsorption processes are found to have a significant role in the overall process and affect the intrinsic reaction rate measurements. On comparing the two modified silicas, it is found that the influence of adsorption in models is less pronounced with the batch-treated material. The decrease in reaction rate effects with the material prepared by a batch process can be attributed to increased quenching of strongly adsorptive sites on the silica surface as a result of prolonged exposure to metal ions in solution. Retention behavior is consistent with a decrease in the influence of hydrogen bonding hydroxyl groups on the batch-treated material.

INTRODUCTION

Complications from solutes reacting during liquid chromatographic separation due to the catalytic activities of adsorbent beds have been observed and summarized by Snyder [1]. While reactions catalyzed by acidic or basic packings can often be eliminated by special surface treatments [2], the presence of active trace metal ions in columns often causes more serious problems in the course of separation, due to complexation and irreversible adsorption [3-6]. We have previously demonstrated how hydroquinone oxidation could be used as a probe reaction for detecting catalytic activity which probably stems from transition metal ions associated with silica columns in high-performance liquid chromatography [7]. The active sites in the column were located through flow-rate and flow direction variations; the redox nature of the active sites were also characterized to some extent. Difficulties with similar reactions during liquid chromatographic separations have also been described for reversed-phase [8] and ion-exclusion [9] columns.

Recently, we have initiated studies of more homogeneous packings containing associated metal ions in columns used as liquid chromatographic reactors (LCRs) in

order to increase our knowledge about the properties of these packings and potential analytical complications, and to investigate further possibilities for utilizing these types of reactors. Because of complications in interpreting reactant and product profiles during kinetic studies, a convenient statistical moment method for parameter estimation was introduced [10]. It is based on the overall elution curve of the reaction chromatogram from the liquid chromatographic reactor and eliminates difficulties which occur when attempting to resolve these curves. Rate constants for a hydroquinone oxidation performed on an *in situ* iron (Fe^{3+})-modified silica column were obtained utilizing this method. The influence of mass transfer processes occurring in the column on reaction rate processes was evaluated and hydroquinone adsorption processes were found to influence reaction rate constant determinations significantly. Two models were developed: model I treated a first-order chemical reaction as the only kinetically controlling process; model II incorporated consideration of finite adsorption and desorption rates for the reactant together with the first-order reaction. The latter showed a better fit to the kinetic data for on-column hydroquinone oxidation on *in situ* iron-modified silica. Other investigators have also addressed the importance of adsorption and desorption mechanisms in chromatographic performance [11–17].

Here, further studies of the hydroquinone oxidation reaction catalyzed by iron (Fe^{3+})-modified silica packing in organic solvents are described to illustrate the kinds of information which can be obtained about packings from using the liquid chromatographic column as a reactor for kinetic studies. Specifically, kinetic analyses based on the two models are applied to an iron-modified silica packing obtained through batch treatment so that comparison can be made with the *in situ* prepared packing as well as to further demonstrate the useful nature of the statistical moment approach for kinetic parameter estimation. Similarities and differences in performance between chromatographic reactors using packings from the batch silica treatment and the previously studied *in situ* treatment are discussed together with variations in retentions of several pertinent materials on the columns.

THEORY

Two models based on the first absolute statistical moment of the overall elution curve (reactant plus product) have been developed for the rate evaluation of a (pseudo-)first-order irreversible reaction in a linear liquid–solid chromatographic reactor [10]. Model I is applicable to an ideal chromatographic reactor situation [18,19] in which the rate of a single chemical reaction determines the overall reactor performance; model II also considers the chemical reaction but incorporates consideration of reactant adsorption and desorption rates which are commensurate with reaction rates. The effects of other kinetic processes on reaction rate evaluation including axial dispersion, external mass transfer resistance across the particle boundary, and intraparticle diffusion have been shown to be negligible [10,19].

Model I: LCR with equilibrium distribution between two phases for both reactant and product

When distribution equilibria between the mobile and stationary phases are established instantaneously and linear isotherms can be utilized for both reactant and

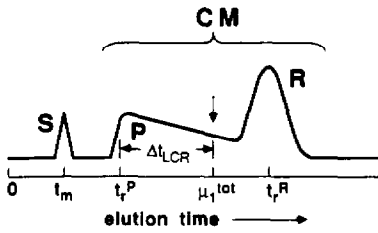


Fig. 1. Hypothetical reactor chromatogram showing parameters of this study: S = standard, R = reactant, P = product, CM = center of mass for the elution profile reactant and product. The first absolute moment for the overall elution curve (μ_1^{tot}) is located at the center of mass of the profile. See text for details.

product, the first absolute moment for the overall elution curve [10] containing both reactant and product, μ_1^{tot} , can be expressed as

$$\mu_1^{tot} = t_r^P + \Delta t_{LCR} \tag{1}$$

Its physical significance together with that of other relevant parameters is illustrated in Fig. 1. Here, t_r^P is the characteristic retention time of the product and Δt_{LCR} represents the shift of the first moment due to liquid chromatographic reaction. The shift can be shown to be equal to

$$\Delta t_{LCR} = \frac{K^R - K^P}{k_{app,I}} [1 - \exp(-k_{app,I}t_m)] \tag{2}$$

where the apparent reaction rate constant for model I is

$$k_{app,I} = k_m + K^R k_{s,I} \tag{3}$$

K^R and K^P are the indicated distribution equilibrium constants for the reactant (R) and product (P) respectively; t_m and k_m are the mobile phase residence time and reaction rate constant respectively; $k_{app,I}$ is the ‘‘apparent rate constant’’ which is the sum of the reaction rates in the mobile and stationary phases for model I while $k_{s,I}$ is the corresponding stationary phase rate constant.

The physical meaning of μ_1^{tot} has been discussed in an earlier development [10]: it is essentially the ‘‘average retention time’’ of the overall elution profile and is located at the center of mass of the P + R distribution as illustrated in Fig. 1. It is expressed in eqn. 1 as the sum of the product retention time and an LCR reaction-dependent term, Δt_{LCR} , which accounts for contributions from the remaining reactant peak and broadening of the chromatogram due to continuous product formation during elution. An analogy to the ‘‘unreacted fraction’’ used in chemical kinetics can be made for the normalized quantity $\Delta \bar{t}_{LCR}$, defined as

$$\Delta \bar{t}_{LCR} = \frac{\mu_1^{tot} - t_r^P}{t_r^R - t_r^P} \tag{4a}$$

$$= \frac{1 - \exp(-k_{app,I}t_m)}{k_{app,I}t_m} \tag{4b}$$

where t_r^R is the characteristic retention time of the reactant and $t_r^R - t_r^P$ of eqn. 4a represents the maximum possible shifting of μ_1^{tot} from its initial position t_r^R when the column is utilized as a separator only and no reaction occurs in the column; then, μ_1^{tot} is equal to t_r^R and $\Delta\bar{t}_{\text{LCR}}$ becomes unity. On the other hand, if the reaction is complete immediately upon reactant introduction to the column and the pulse is eluted as a single product peak, μ_1^{tot} is equal to t_r^P and $\Delta\bar{t}_{\text{LCR}}$ becomes zero. These correspond to a zero and infinite k_{app} value respectively, which also results in $\Delta\bar{t}_{\text{LCR}}$ values of 1 and 0 in eqn. 4b. In the liquid chromatographic reactor operation, this dimensionless group has a value between zero and unity and relates to the percentage or extent of reaction occurring inside the column. Thus, it relates to the fraction of unreacted species often used in chemical kinetics and reactor design, *i.e.* $(1 - X)$, where X is the fractional conversion [20].

Model II: LCR without equilibrium distribution between two phases for the reactant

When reactant adsorption and desorption rates are commensurate with chemical reaction rates and other mass transfer processes have negligible effects on reaction rate, the overall first absolute moment for model II can again be written in the form of eqn. 1 and parameters illustrated in Figure 1 are still applicable, but with the value of Δt_{LCR} now having a different dependence on kinetic parameters [10]:

$$\Delta t_{\text{LCR}} = \frac{K_{\text{ad}}^R}{(1 + k_{\text{s,II}}/k_{\text{d}})} - K^P \frac{1}{k_{\text{app,II}}} [1 - \exp(-k_{\text{app,II}}t_m)] \quad (5)$$

$$k_{\text{app,II}} = k_m + K_{\text{ad}}^R \frac{k_{\text{s,II}}}{1 + k_{\text{s,II}}/k_{\text{d}}} \quad (6)$$

Now, K_{ad}^R is the adsorption equilibrium constant for the reactant ($=k_a/k_d$, where k_a and k_d are the adsorption and desorption rate constants), and $k_{\text{app,II}}$ and $k_{\text{s,II}}$ are the apparent and stationary phase rate constants respectively of model II. Although adsorption and desorption rate constants cannot be determined directly from eqn. 5 due to coupling between these kinetic parameters in the expression, model II can be distinguished from model I on the basis of the different dependences of Δt_{LCR} on the stationary reaction rate constant in the two models.

Utilization of μ_1^{tot} in rate evaluation can readily overcome the problem resulting from overlap between reactant and product profiles [21]. The use of the total elution curve also eliminates a need for applying internal or external standard methods together with associated complications. In practice, μ_1^{tot} can be measured directly from the experimental elution curve of a reaction chromatogram as a function of the mobile phase residence time.

Consequently, Δt_{LCR} is calculated from eqn. 1 with its dependence on t_m shown in eqns. 2 and 5 for models I and II respectively. By varying flow rates in the LCR system, data at different t_m values are generated and kinetic parameters can then be estimated by a non-linear regression routine and compared for each model.

EXPERIMENTAL

Liquid chromatographic reactor system

The standard liquid chromatographic system employed here as a liquid chromatographic reactor, incorporated a Waters 590 solvent delivery pump (Milford, MA, USA), an LDC/Milton Roy SpectroMonitor D absorbance detector (Riviera Beach, FL, USA) set at the wavelength of 267.5 nm, and a special glass column (10 cm × 3 mm I.D., Omnifit, Atlantic Beach, NY, USA) to minimize potential contact with metal while permitting observation of color changes from silica surface modification by ferric ions. The assembly and other details have been described elsewhere [10]. Digitized chromatographic signals were acquired and stored using a Hewlett-Packard 3396A integrator equipped with a 9114A disc drive (Palo Alto, CA, USA). Data processing for conversion of the reactor chromatogram signals to the first absolute moment (see Fig. 1) was also performed in this system which possesses a BASIC language capability.

Batch procedure for preparing iron-modified silica

Packing material (Spherisorb S10W 10 μm silica gel from Phase Separations, Norwalk, CT, USA) was dried in an oven (150°C) overnight. It was then equilibrated with a buffered isopropanol solution [0.04 M potassium acetate + 1% (v/v) acetic acid] in an erlenmeyer flask on a stirrer for 5 h before washing with neat isopropanol several times. This activation step was needed for effective metal doping onto the silica surface [22]. Subsequently, the silica sample was treated with a 2.72 mM FeCl_3 -isopropanol solution overnight during which time the coated silica slurry attained a light yellow color. This modified silica was then centrifuged and washed with isopropanol to remove free ferric material, and dried under nitrogen at 50°C. The final product was slurry-packed into the glass column with an in-house constructed slurry packing apparatus.

A similar procedure for *in situ* modification of the silica surface by pulse injections of ferric ions into a pre-packed silica column has been described earlier [10]. This procedure also provided a column of uniform color comparable to the one from slurry packing. The pulse injection technique with a glass column allows observation of color change as the yellow zone develops along the column. In this particular situation, it also eliminates unnecessary metal contacting in the pump. Ferric chloride can be a strong hydrometallurgical leaching agent under some conditions. For other types of surface modification, one might treat columns *in situ* by continuously pumping solutions containing modifiers. Results from an inductively coupled plasma (ICP) emission spectrometer analysis showed an iron loading of *ca.* 0.1% (w/w) on silica packing for both batch-treated and *in situ* samples.

Chromatographic reactor study and reagents

The kinetic study for hydroquinone oxidation in the batch-treated iron/silica column was conducted at temperatures between 20 and 40°C and flow-rates between 0.75 and 1.5 ml/min. Temperature control was obtained in the same way as in the *in situ*-treated column using a column jacket [10]. The mobile phase used for the batch-treated column was a 4% solution of *tert.*-butanol in hexane, while the solvent composition was 8% *tert.*-butanol/hexane mixture with the *in situ*-modified column.

Capacity factors of hydroquinone and benzoquinone were measured for the silica column before and after *in situ* treatment as well as for the batch-treated column. The column void volume was determined with a toluene standard and corrected for the extra-column volume. All solvents and chemicals used in this study were purchased from Baxter (McGaw Park, IL, USA) and Aldrich (Milwaukee, WI, USA).

RESULTS AND DISCUSSION

A representative series of liquid reactor chromatograms at various flow rates for the iron-catalyzed hydroquinone oxidation in the batch-treated silica column are illustrated in Fig. 2 for both 25 and 35°C. The first absolute moment of the overall elution profile μ_1^{tot} for a particular flow-rate can be obtained directly from a reactor chromatogram with the data processing system described earlier and the equation

$$\mu_1^{\text{tot}} = \frac{\sum_{t=t_1}^{t_2} [C^{\text{R}}(t) + C^{\text{P}}(t)]t\Delta t}{\sum_{t=t_1}^{t_2} [C^{\text{R}}(t) + C^{\text{P}}(t)]\Delta t} \quad (7)$$

where $C^{\text{R}}(t)$ and $C^{\text{P}}(t)$ are the reactant and product concentrations at elution time t ; these quantities correspond to the detector response with the wavelength set at 267.5 nm where the absorptivities of hydroquinone reactant and benzoquinone product are equal. Here, the summations cover the time range of the total elution curve between t_1 and t_2 , and are calculated at the data acquisition speed of 20 points/s ($\Delta t = 0.05$ s). Now, data for the normalized μ_1 shift, $\Delta \bar{t}_{\text{LCR}}$, can be calculated from eqn. 4a and plotted against flow-rate for various reaction temperatures as shown in Fig. 3 for the indicated reaction chromatogram series. The normalized value at the ordinate resembles the fraction of reactant remaining in the effluent stream ($1 - X$) as explained

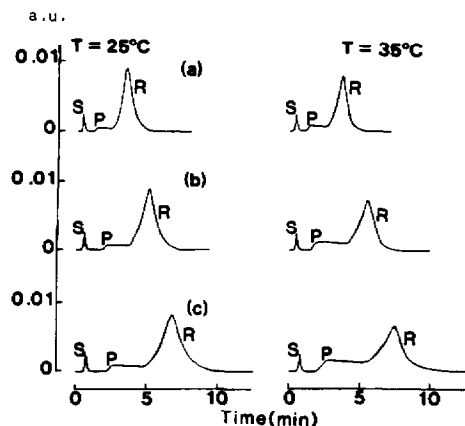


Fig. 2. Series of liquid reactor chromatograms for hydroquinone oxidation catalyzed by batch-treated iron/silica at 25 and 35°C. R = Hydroquinone reactant; P = benzoquinone product; S = toluene standard; mobile phase: 4% *tert.*-butanol in hexane; sample: 20 μl of 0.72 mM hydroquinone; wavelength: 267.5 nm. Flow-rates: (a) 1.5 ml/min; (b) 1.0 ml/min; (c) 0.75 ml/min.

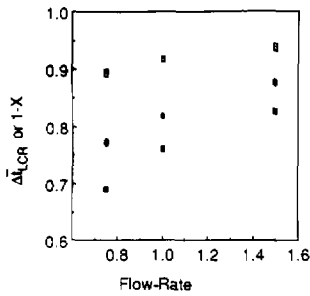


Fig. 3. Dependence of Δt_{LCR} on mobile phase flow-rates (in ml/min) at various column temperatures; operating conditions same as Fig. 2. \square = 25°C; \blacklozenge = 35°C; \blacksquare = 40°C.

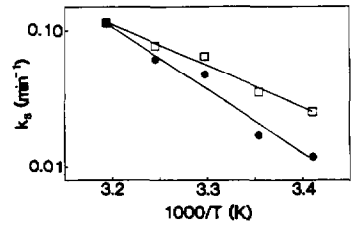


Fig. 4. Arrhenius plots of stationary phase reaction rate constants versus temperatures for models I (\square) and II (\bullet) in the batch, iron-modified silica column.

earlier and can be used to study the effects of reaction time and temperature on extent of reaction occurring in a column. The reaction time for the hydroquinone oxidation in the column increases with decreasing flow-rate, and results in higher conversions as shown in the series of chromatograms of Fig. 2. This gives larger X values, and thus lower Δt_{LCR} values as illustrated in Fig. 3 for all temperatures. Also shown in Fig. 3 is the effect of increasing reaction temperature; the resulting higher reaction rate gives a lower Δt_{LCR} value for the same flow-rate. At the limit of an infinite flow-rate which corresponds to no chemical reaction in the column ($X = 0$), the ordinate values should approach unity for all temperatures.

Reaction kinetic parameter estimation

Hydroquinone oxidation kinetic data analysis for the batch-treated column can be performed in a manner resembling that of the *in situ* case. Neglecting any uncatalyzed mobile phase reactions, eqns. 2 and 5 become [10]

$$\Delta t_{LCR,I} = \frac{1 - (K^P/K^R)}{k_{s,I}} [1 - \exp(-K^R k_{s,I} t_m)] \tag{8}$$

and

$$\Delta t_{LCR,II} = \left(\frac{1}{k_{s,II}} - \frac{K^P}{k_{app,II}} \right) [1 - \exp(-k_{app,II} t_m)] \tag{9}$$

Now, $k_{s,I}$ for Model I and $k_{s,II}$ and $k_{app,II}$ for Model II can be fitted by a non-linear regression routine. The kinetic parameters in eqns. 8 and 9 were determined with a VAX 11/785 computer using the GREG (general regression) program, a FORTRAN package of the least-square algorithm to estimate the parameters of a user-defined model developed by Stewart [23]. The stationary phase rate constants for models I and II determined by GREG are plotted against reaction temperature in Fig. 4 for the batch-treated column. In Fig. 4, it can be seen that values of k_s for model I deviate from those from model II at low temperatures but give more comparable values at higher

TABLE I

COMPARISON OF KINETIC PARAMETERS FOR STATIONARY PHASE RATE CONSTANTS FOR BATCH AND *IN SITU* TREATMENTS

	Kinetic parameter ^a	Batch treatment	<i>In situ</i> treatment [10]
Model I	$\ln k_s(T_B)$ (min^{-1})	-3.096	-1.208
	E_s (kcal/mol)	13.22	4.10
Model II	$\ln k_s(T_B)$ (min^{-1})	-3.592	-2.343
	E_s (kcal/mol)	20.06	13.04

^a Arrhenius relation: $\ln k_s = \ln k_s(T_B) - (E_s/R)(1/T - 1/T_B)$, where R is the gas constant and T_B is a base temperature (= 303.15 K); $k_s(T_B)$ is the stationary phase reaction rate constant at 303.15 K and E_s is the activation energy for stationary phase reaction.

temperatures (*ca* 40°C). This reflects the importance of the effect of finite hydroquinone sorption rates at low temperatures. The result is consistent with the *in situ*-treated case since a greater contribution to the elution curve from unreacted hydroquinone reactant is expected at low temperatures where the conversion is low. Thus, a general hydroquinone adsorption effect on rate evaluation is present in the modified silica packings generated for both treatments.

Values of the fitted Arrhenius kinetic parameters in the range of experimental reaction temperatures for the stationary phase rate constants in the two models can also be compared for the batch and *in situ* treatments; these are listed in Table I. The deviations for both kinetic parameters, E_s and k_s , are significantly less for the batch-treated packing than for the *in situ*-treated packing as shown in Table I. This is an indication that the contribution of the hydroquinone adsorption mechanism on intrinsic kinetic evaluation is less important with the former. Table I also indicates a difference in the catalytic activity of the iron-modified silica produced from these two treatments. The *in situ* treated material is more catalytically active as reflected in the rate constant values. Possible explanations for variations between the two iron-modified silica packings are discussed below.

Model discrimination

"Goodness" of model fits to the experimental data from the *in situ*-treated

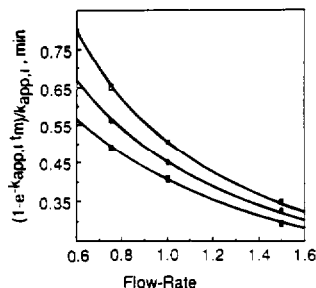


Fig. 5. Simulation curve comparison for Δt_{LCR} (corrected to account for the kinetic contribution alone, see eqn. 2) with experimental data in the batch-treated silica column for model I: \square = 25°C; \blacklozenge = 35°C; \blacksquare = 40°C. Flow-rate scale in ml/min.

column were examined earlier by calculating predicted responses from estimated parameters as a function of flow-rates at several temperatures [10]. For that packing, model II showed superiority over model I under operating conditions of high flow-rates and low temperatures where adsorption of hydroquinone is important. A similar analysis was conducted for the column packed with batch-treated material using model I as shown in Fig. 5. Analysis with model II did not improve the results significantly. Here then, kinetic evidence from parameter estimation for a significant adsorption effect is less obvious since both models can provide relatively good data fit under all operating conditions. The different behavior of the column packings resulting from the batch and *in situ* procedures can be related to variations in the silica surface properties during the treatments.

Longer and milder contacting treatment of the batch reaction apparently tends to generate a more homogeneously modified silica sample than the *in situ* treatment. The resulting product is likely to contain fewer strongly adsorptive sites on the silica surface, including isolated and vicinal silanol groups as noted by others [24–26]. It is quite likely that these associated hydroxyl groups are responsible for the strong adsorption of hydroquinone and thus, for the greater deviation between the two models in the *in situ* case. This is consistent with the results from comparing retention behavior of the samples (capacity factors) in the two columns, as shown in Table II. Less resolution of hydroquinone from benzoquinone was achieved on packings prepared by the batch procedure using a mobile phase of 8% of *tert.*-butanol in hexane. While retentions of benzoquinone were comparable on both packings, hydroquinone was retained significantly less on the batch-treated packing. This can be explained by a significant loss of hydrogen bonding surface silanol groups (especially vicinal groups) during the batch reaction; these and other associated groups might give longer hydroquinone retention [24]. With the loss of hydroquinone retention relative to benzoquinone, it became appropriate to use an eluting solvent with only 4% *tert.*-butanol to achieve resolution. Additional support for this view is the fact that the batch-treated column gives reaction chromatograms showing less tailing for the hydroquinone reactant peak than the *in situ*-treated column (even with the weaker mobile phase).

A likelihood ratio test [27,28] can be utilized to discriminate between the two “nested” models in order to determine which provides a better fit for the hydroquinone oxidation kinetic data on a statistical basis. The likelihood ratio test is based on the principle of variance ratio, usually known as the *F* ratio, for analysis between a full and

TABLE II
CAPACITY FACTORS FOR THE HYDROQUINONE OXIDATION SYSTEM (8% *tert.*-BUTANOL IN HEXANE AT 25°C)

Column	Benzoquinone	Hydroquinone
Silica before treatment	1.55	5.55
<i>In situ</i> iron treatment	1.27	3.01
Batch iron treatment	1.31	2.26
	(1.75) ^a	(8.43) ^a

^a Values for the mobile phase of 4% *tert.*-butanol in hexane.

TABLE III
EXTRA SUM OF SQUARE ANALYSIS^a FOR MODEL DISCRIMINATION

Packing treatment	Source	Residual sum of squares (RSS)	Degrees of freedom (n_f)	Mean square (RSS/ n_f)	Mean square ratio
<i>In situ</i>	Model I (1 parameter)	0.04690	11	0.00018	250
	Model II (2 parameters)	0.00182	10		
	Extra parameter	0.04508	1		
Batch	Model I (1 parameter)	0.01981	11	0.00044	35.0
	Model II (2 parameters)	0.00444	10		
	Extra parameter	0.01537	1		

^a Kinetic data at 35°C for *in situ* (CYJ4-34) and batch (CYJ4-44) treatments.

a partial model. Results of a representative calculation for examination of the effect of addition of the extra parameter in model II are illustrated in Table III for the two iron treatments. In Table III, the mean square can be determined by dividing the degrees of freedom into the residual sum of squares for the full model as well as for the extra kinetic parameter added into the partial model. Then, the calculated mean square ratio value between the extra parameter and the full model is compared with the F ratio from statistical distribution tables at proper degrees of freedom ($n_f = 1$ for the extra parameter and 10 for the full model) and a chosen probability α that the test is significant (e.g. $F = 10.0$ and 1.5 for $\alpha = 99\%$ and 75%, respectively). If the calculated ratio is greater than the table value, the extra parameter should be retained and the full model is statistically better than the partial model; otherwise, one should accept the partial model. Results from Table III indicate that the extra parameter is important in both treatments, but particularly for the *in situ* packing. The mean square ratios from some data sets are plotted against temperature in Fig. 6. It is found that the test ratios are larger than standard F values with $\alpha = 99\%$ in most cases and even more so when $\alpha = 75\%$ is chosen. This implies that the extra parameter in model II to describe the reactant adsorption and desorption process is statistically important and model II is a better representation of the LCR system than model I in general, although the batch-treated packing shows less of this effect especially in comparing conversions with flow (Fig. 5). A trend of decreasing mean square ratio values as temperature increases can also be detected in Fig. 6. Large F values at low temperatures guarantee

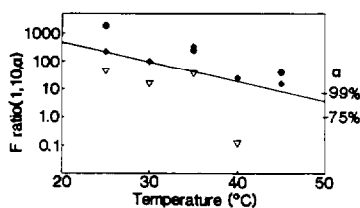


Fig. 6. Results of the likelihood ratio test between model I and model II at various reaction temperatures. Filled symbols (● = CYJ4-34; ◆ = CYJ4-47) = *in situ* treatment, open symbols (▽ = CYJ4-44) = batch treatment.

the superiority of model II over model I there since only a small fraction of reactant was converted to product and the hydroquinone adsorption process is a controlling process. At higher temperatures, a larger portion of hydroquinone was converted to benzoquinone and the importance of the reactant adsorption rate relative to the chemical reaction is diminished. The result is smaller F values so that the advantage of using model II over model I at higher temperatures becomes less significant especially with the batch treatment.

CONCLUSIONS

A statistical moment approach based on an overall elution curve has been applied successfully for the on-column hydroquinone oxidation catalyzed by iron-modified silica. Results from batch and *in situ* procedures for modifying the silica surface with ferric ions are compared. A reactor model which incorporates consideration of finite reactant adsorption and desorption processes generally shows a better fit to the experimental data than a simple model where only chemical reaction is considered. The former is particularly advantageous at low temperatures where the reactant species is predominant in the chromatogram. The *in situ*-treated sample shows larger discrepancies between the two models and indicates a more significant effect of hydroquinone adsorption on reaction rate evaluation than the batch-treated one. Differences in the performance as a result of the two treatments can be attributed to variations in the loss of hydrogen bonding silanol groups of the treated samples. Further investigations of modified silicas of the type described here are continuing in our laboratory.

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