AN ABSTRACT OF THE THESIS OF

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Title: Modeling the Conversion of Arabinose to Furfural

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Robert D. Sproull

Hemicellulose hydrolyzate contains many carbohydrate fractions, the most abundant being xylose, arabinose, and glucuronic acid. Under mild acid conditions (0.025 - 0.10 M sulfuric acid) and high temperatures (140°C to 200°C) the first two components form furfural through a series of dehydration reactions. Unlike xylose and arabinose, glucuronic acid must first undergo a decarboxylation reaction before the dehydration steps to form furfural. The kinetics for the reaction of xylose to furfural have been studied extensively (Root et al., 1959 and Sproull, 1986). Some researchers have considered the kinetics of arabinose degradation (Bott et al., 1932; Hurd et al., 1932; Hughes et al., 1939; Saeman, 1945), however, the rate constants for the dehydration of arabinose to furfural have not been accurately modeled to fit an Arrhenius expression.

The scope of this work was to model the kinetics for the formation of furfural from arabinose in the aqueous phase using the three-constant Dunlop model. The conversion of arabinose was found to follow a first-order reaction. Some experimental runs were made in the presence of an extraction solvent, ortho-nitrotoluene. In this case furfural concentrations were determined in both phases. The use of the extraction solvent is to protect the forming furfural from further acid degradation. The solvent to water ratio in these experiments was two.

Predicted furfural concentration profiles (aqueous and solvent phases) were compared to the experimentally determined values assuming that the process was diffusion limiting. The two profiles were in good agreement with each other up to and including the maximum furfural concentration. At times after the maximum furfural concentration, the predicted profiles slightly overestimated the experimental furfural concentrations. A short study was also made to consider the possibility that furfural degradation may occur in the solvent phase (o-nitrotoluene) which would decrease the furfural yield. In this case, the decomposition of furfural in the solvent phase was negligible.

Modeling the Conversion of Arabinose to Furfural

by

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MODELING THE CONVERSION OF ARABINOSE TO FURFURAL

CHAPTER 1

INTRODUCTION

Furfural is most frequently used in the production of resins, lubricants and as the precursor for other chemicals such as THF, furfuryl alcohol, and maleic acid (Wenzl et al., 1970; Sproull, 1986 and Goldstein, 1986). It is also useful as a solvent in the selective extraction of petroleum chemicals (Kemp et al., 1940).

The production of furfural from pentoses, was first reported in the early nineteenth century. It has been only in the latter part of this century that a kinetic mechanism has been proposed for its formation in acidified xylose solutions.

An abundant source of pentoses can be obtained from the hemicellulose component of various hardwood, softwood and plant residues. Typically, the majority of the hemicellulose is composed of xylose, with smaller fractions of arabinose, glucuronic acid, mannose, and glucose (Goldstein, 1986). The exact compositions depend on the carbohydrate source itself.

The kinetics for the acid catalysis of xylose to furfural has been studied extensively (Root et al., 1959 and Sproull, 1986). However, the kinetics for the dehydration of arabinose need to be modeled in an Arrhenius expression using the Dunlop three-constant model.

Arabinose --> Intermediates --> Furfural --> Degradation Products

Intermediate + Furfural ----> Resin

Eventually the kinetics for the dehydration of glucuronic acid to furfural will need to be determined.

To reduce the amount of furfural degradation, it has been proposed to remove the furfural from the aqueous phase by either steam distillation or extraction into a suitable water-insoluble solvent with a high furfural distribution coefficient (Harris et al., 1961; Lazero et al., 1986). For this work, extraction into o-nitrotoluene was chosen because the alternative choice leads to the high cost of steam distillation of the furfural-water azeotropic mixture.

CHAPTER 2

THEORY

2.1 Conversion of Arabinose to Furfural

Historically, the discovery of furfural was first noted in the early nineteenth century when a yellow oil develop while attempting to produce formic acid from the oxidation of various sugar solutions. The name originates from the roots 'furfur' meaning bran and 'oleum' meaning oil. Of course the 'al' suffix now used, identifies it as an aldehyde.

Not until after World War I did furfural production reach an industrial scale, when in 1922 Quaker Oats began production utilizing oat hulls as a feed stock.

This paper attempts to model the kinetics for the conversion of arabinose to furfural in the aqueous phase by applying the same three constant model past researchers have used to explain the conversion of xylose to furfural (Root et al., 1959; Sproull, 1986).

$$X \xrightarrow{k_1} I \xrightarrow{k_1'} F \xrightarrow{k_2} D$$

$$I + F \xrightarrow{k_3'} P$$

where

X = xylose

F = furfural

I = Intermediate

D = Degradation Products

P = Polymerization Resins

The exact mechanism for this acid catalyzed reaction has not yet been deduced, however, Hurd et al. (1932) have suggested the following multi-intermediate steps illustrated in Figure 2-1.

The degradation of xylose has been shown to follow a first-order rate law (Hurd et al., 1932; Dunlop, 1948; Root et al., 1959; Sproull, 1986)

$$\frac{d[X]}{dt} = -k_1[X] \qquad (2\text{-}1)$$

Since arabinose is a geometrical isomer of xylose one should expect a similar result

$$\frac{d[A]}{dt} = -k_1[A] \qquad (2\text{-}2)$$

However, one might suspect that the reaction rate constants, k_1 should differ.

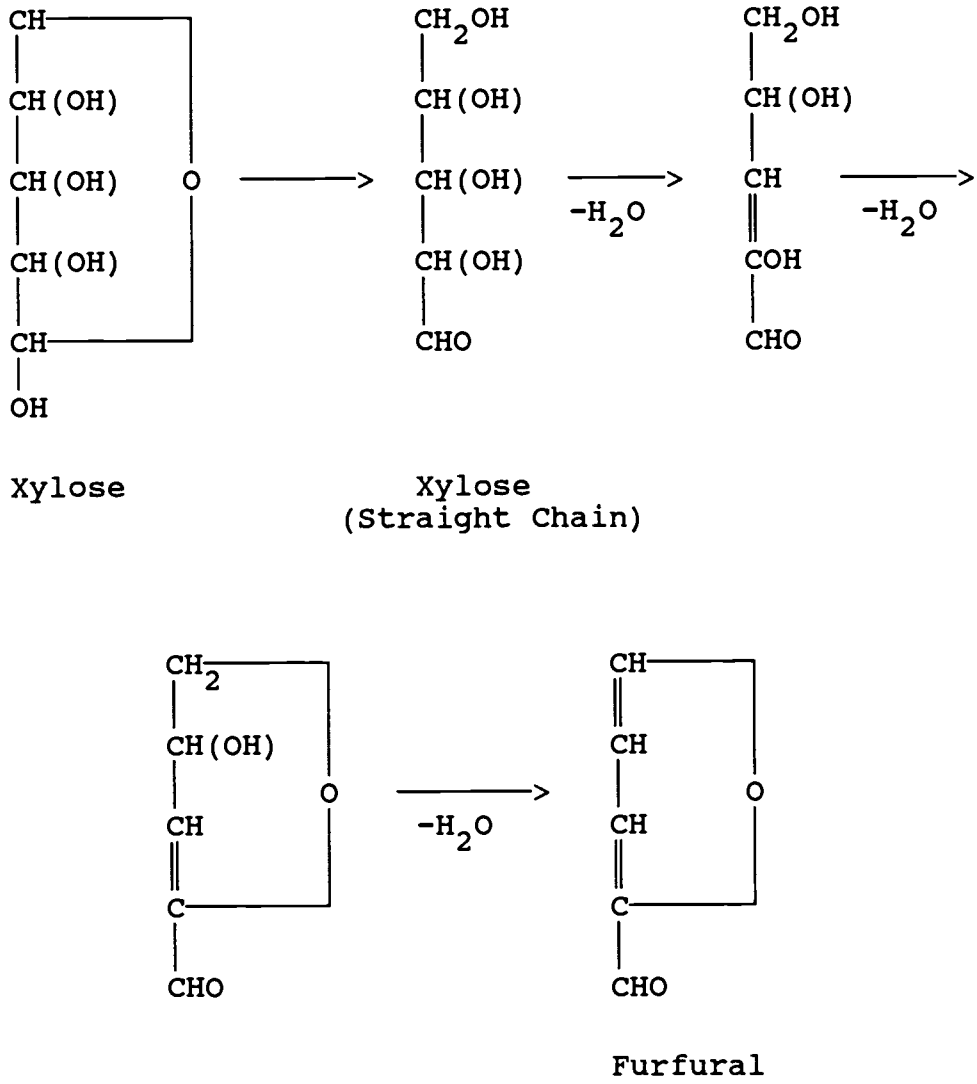

Figure 2-1

Proposed Mechanism for the Dehydration of Xylose to Furfural

This result is most likely due to the different mutarotation velocities of each sugar, since a key step in the reaction may be the formation of the open chain aldehyde from the cyclic hemiacetal (Dunlop et al., 1953)

The rate of the disappearance of arabinose in acidified solutions has been studied briefly by several people, but at limited acid concentrations and temperatures (Bott et al., 1932; Saeman, 1945). Others have only evaluated the potential furfural yield from arabinose ignoring the kinetics (Pervier et al., 1923; Hurd et al., 1932; Hughes et al., 1939). In all of the above cases dilute sulfuric acid or hydrochloric acid was used as the catalyst and the furfural collected by steam distillation. Thus, even at this early time it was realized that the furfural must be remove from the acid environment in order to achieve high yields.

Saeman and Bott have reported specific rate constants for the degradation of arabinose in dilute sulfuric acid and noted them to be slightly smaller than the corresponding rate constants for xylose under the same reactions conditions. Their results suggest that arabinose is more stable than xylose in acidic solutions.

To complete the three-constant model, the rate constant k_2 has been determined as a function of acid concentration and temperature, (Williams et al., 1948; Dunlop, 1948; Sproull, 1986) and will be applied in this

new model. This leaves the kinetic constant k_3, which will be evaluated numerically.

Several steps need to be explained at this point. First, consider a model similar to the one developed by Root et al. for xylose (1959).

$$A \xrightarrow{k_1} I \xrightarrow{k_1'} F \xrightarrow{k_2} D$$

$$I + F \xrightarrow{k_3'} P$$

where

A = arabinose

I = intermediate species

F = furfural

P = polymerization products

D = degradation products

$$r_I = \frac{d[I]}{dt} = k_1[A] - k_1'[I] - k_3'[I][F] \qquad (2\text{-}3)$$

$$r_F = \frac{d[F]}{dt} = k_1'[I] - k_2[F] - k_3'[I][F] \qquad (2\text{-}4)$$

The existence of the intermediates have been shown to be short-lived and equation (2-3) can be rewritten assuming a small steady-state concentration of I. HPLC analysis of the reaction mixtures confirmed the presence of only a small concentration of unidentifiable intermediates. With $r_I = 0$ equation 2-3 is solved for [I].

$$[I] = \frac{k_1[A]}{k_1' + k_3'[F]} \qquad (2\text{-}5)$$

Since the presence of furfural is observed, the destruction of furfural must be considerably slower than its formation, therefore one can make the approximation that,

$$k_1' >> k_3'[F]$$

and the expression for equation (2-5) reduces to,

$$[I] = \frac{k_1[A]}{k_1'} \qquad (2\text{-}6)$$

Substituting equation (2-6) into equation (2-4) gives the final rate expression for furfural.

$$r_F = k_1[A] - k_2[F] - k_3[A][F] \qquad (2\text{-}7)$$

where the kinetic constant k_3 is defined as,

$$k_3 = \frac{k_1 k_3'}{k_1'} \qquad (2\text{-}8)$$

All of the kinetic constants are modeled by the

Arrhenius expression,

$$k_i = k_{i_0}[H_2SO_4]^a \exp[-E_i/RT] \qquad (2\text{-}9)$$

where

k_{i_0} = the pre-exponential factor (min^{-1})

$[H_2SO_4]$ = catalyst concentration (M)

a = exponential factor

E_i = activation energy for the reaction (cal/g-mol K)

R = gas constant (1.987 cal/g-mol K)

T = temperature (K)

At elevated temperatures the concentration of the sulfuric acid is approximately the same as the concentration of the hydrogen ion, $[H^+]$. This is because the first proton from sulfuric acid is completely dissociated, whereas, the second dissociation constant is on the order of 10^{-2} and decreases exponentially as a function of increasing temperature. In effect, the dissociation of the second proton from sulfuric acid is insignificant and has no effect on the pH of the solution (Dean, 1985).

The degradation of furfural in the presence of heat and acids has been studied (Dunlop et al., 1940, 1946,

1948). The stability in the absence of acids has also been demonstrated. Only a few tenths of a percent of furfural was destroyed while heated at 180°C for 185 hr and 3 - 5 % destroyed at 230°C for 85 hr (Dunlop, 1948). Industrially, furfural will never be subjected to such harsh conditions and thus can be assumed to be nonreactive in the absence of acids.

2.2 Two-Phase Kinetics

There are three choices for the recovery of furfural from the acidified aqueous phase; solvent extraction, adsorption on solids and steam distillation. The first method is the most economically feasible choice, although all three will give high overall furfural yields.

Extraction of the furfural into a solvent phase with a high furfural distribution coefficient (m) can be modeled as a two phase system with the assumption that both liquids are totally immiscible.

$$m = \frac{[F]s}{[F]aq} \qquad (2\text{-}10)$$

where

[F]s = furfural concentration in solvent phase at equilibrium (M)

[F]aq = furfural concentration in the aqueous phase at equilibrium (M)

Two processes are taking place, first, the formation and degradation of furfural in the aqueous phase followed by the mass transfer of furfural from the aqueous phase to the solvent phase. If the interfacial area is increased by agitating the two phases, one can assume that instantaneous mass transfer occurs. Hence, the mass transfer of furfural into the solvent phase is limited by the reaction rate for the formation of furfural. This

represents the ideal case when most of the furfural is removed from the aqueous phase, thus reducing the amount degraded. The other extreme is when the process is diffusion-controlling. In this case the slow-step is the rate of diffusion of furfural from the aqueous phase into the solvent phase. The last possibility is when the process is neither reaction or diffusion-controlled, in which both effects are significant.

2.3 Chromatographic Methods

The analysis of monosaccharides can be performed by two different methods, gas-liquid chromatography, or liquid chromatography. The former requires the preparation of volatile sugar derivatives. Examples are the trimethylsilyl ether derivative (Brower et al., 1966), and the reduction of the sugar to its corresponding alditol with subsequent acylation using acetic anhydride (Borchardt et al., 1970).

The disadvantages of GC analysis are the time consuming steps required to prepare the derivatives and the fact that the derivative reactions are never quantitative (Palmer, 1975). In some cases more than one derivative can be prepared from a single sugar using the same reagent (Morita et al., 1978). The main advantage of GC analysis is that it allows a fast analysis of the unknown mixtures.

Liquid chromatography allows the analysis of the non-volatile carbohydrates without the preparation of derivatives. The use of a refractive index detector allows accurate and efficient analysis of the sugar solutions with complete recovery of the sample. Today, the resolution of various monosaccharides by LC methods is comparable to that obtained by GC analysis (Palmer, 1975). Recently new columns have been developed which can operate

at high eluent flow rates and are able to resolve multicomponent sugar solutions in 15 min or less. Analysis for furfural could be performed by either GC or HPLC methods, but since arabinose (a nonvolatile component) is present in significant amounts with the furfural, the later method was preferred.

Most carbohydrate HPLC columns used in other research efforts required an external column heater (Pettersen et al., 1984; Wentz et al., 1982; Paice et al., 1982), while other columns (particularly those made by Waters) were operative at room temperature (Palmer, 1975). The Biorad columns which operated at elevated temperatures were packed with a lead(II) cation-resin material and typical flow rates varied from 0.5 to 0.6 ml/min. The mobile phase was in most cases distilled, deionized and degassed water or were various compositions of water and acetonitrile.

One last note should be made regarding the aqueous phase analysis using the HPLC system. The particular carbohydrate columns used were composed of a Ca^{+2} based resin. Carbohydrate and aromatic compounds are separated on the basis of the hydrophilic interactions between the bound Ca^{+2} ions and the polar side groups of the mobile phase and sample molecules. There is competition between the solvent molecules and the sample molecules for the Ca^{+2} sites. Molecules which have stronger attractive

forces for these sites will be retained for a longer time. For hexoses the most strongly retained compounds are those with adjacent axial-equatorial-axial OH groups (Angyal, 1981). A similar analysis is possible with the pentose sugars, thereby explaining the different retention times for the geometrical isomers xylose and arabinose.

CHAPTER 3

EXPERIMENTAL APPARATUS AND PROCEDURES

3.1 Aqueous Phase Kinetics

Aqueous-phase kinetic studies were performed in ten stainless steel reactor bombs constructed from 3/4" ID by 1.6" long swagelok weld fittings which were capped on one end and plugged and welded on the other. The interior was bored out to a constant diameter so that the internal volume was approximately 11 ml.

The reaction bombs were filled with 9.3 ml of a solution of known arabinose and sulfuric acid concentration. This volume allowed for the volume expansion of the liquid at reaction temperatures (140 - 200°C) with the properties of the solution assumed to be that of water since the solutions were very dilute. A volumetric pipet was used to measure the appropriate volume. A thread lubricant was applied to the threads of the swagelok fitting to prevent heat damage. The swagelok caps were then fastened onto the bombs by a torque wrench applying a maximum torque of 70 ft-lb, which was high enough to prevent vapor from escaping and yet not strip the threads.

The reaction vessels were spaced apart from

each other and in an uptight position inside a stainless steel basket which ensured uniform heating. The basket was then placed in a preheated Lauda model KS20D high temperature oil bath. This bath is equipped with a digital temperature scale accurate to within ± 0.1°C when the oil bath is covered. The high temperature oil used in the bath was a high boiling point (390°C) aromatic hydrocarbon oil, dibenzyl toluene, able to withstand temperatures up to 230°C without creating a fire hazard. Since large amounts of vapor were given off at temperatures greater than 180°C, the entire heating unit was placed under a ventilated hood.

The reaction vessels were heated for a specified time, then removed from the oil bath and immediately quenched in a tub of ice water. After reaching room temperature, the reaction mixture was removed from the bombs and filtered through a Gelman filter apparatus using 0.45-μm cellulose acetate filters and collected in clean HPLC autosampler vials for future analysis. It took approximately 1 ml to fill each vial.

3.2 Two-Phase Kinetics

For the two-phase reaction experiments 3.1 ml of the solution of known arabinose and sulfuric acid concentration were added to 6.2 ml of o-nitrotoluene in the reaction vessel. Once again the volumetric pipets were used to measure the correct volume of each. The reaction mixtures were heated and quenched in the same manner discussed in the previous section. Upon reaching room temperature, the mixtures were emptied into 3/4" OD by 3.0" long glass vials and allowed to equilibrate at room temperature for at least 24 hr. At this point the two phases were immediately separated using disposable pipets, and stored in separate glass vials for future analysis. Corrections were made to calculate the furfural concentrations in both phases at the reaction temperatures. Analysis for arabinose and furfural in the aqueous phase was performed by a High Performance Liquid Chromatograph (HPLC) system purchased from Beckman Instruments Inc. Liquid chromatography was chosen because of the presence of the non-volatile sugars, sugar derivatives, and resins in the solution. Analysis for furfural in the solvent phase was performed by gas chromatography.

3.3 Analysis of the Aqueous Phase

The equipment for this experimental work consisted of an Altex model 156 Refractive Index Detector, a Beckman model 110B solvent delivery system, a Spectra Physics model SP8780 XR autosampler, a Beckman model 427 Integrator, a Biorad HPLC column heater, and two Altex Spherogel Ca^{+2} resin, 6.5mm ID by 300mm long, columns. The RI detector was chosen over the UV detector because of the more accurate results of the former, when applied to carbohydrate solutions. The sensitivity of the RI detector for furfural was very high; able to detect furfural concentrations as low as 1.0 mM. An in-line filter apparatus, which utilized disposable 0.45 μm filters, was installed in front of the carbohydrate column to remove any solid particles and prevent damage to the column packing. The disposable filters were replaced when the solvent pump gauge read a pressure greater than 1200 psig. This corresponded to changing the filters every week when the system was under daily use.

The mobile phase was distilled, deionized, and degassed water flowing at a constant rate of 0.6 ml/min. The carbohydrate column was heated to 90°C and the RI detector was allowed to warm up for 45 min. During this time water was flowing through the entire system. After the column has reached both thermal and chemical

equilibrium, the pressure drop over the column was on the average 800 psig as displayed by the solvent pump gauge. This value was considered acceptable because the maximum pressure that the column could withstand was 1000 psig. Occasionally, the carbohydrate column needed regenerating. This was accomplished by running a 5 mM solution of $Ca(NO_3)_2$ through the column overnight at a flow rate of 0.1 ml/min.

The filtered reaction samples were loaded into the autosampler carousel and the model SP8780 XR autosampler was programmed to inject 20 μL samples at 30-min intervals until all of the samples were analyzed. The respective absorbance readings were recorded by the Beckman 427 integrator on heat sensitive paper. The average retention times for furfural and arabinose are 22.0 and 9.0 min, respectively. The attenuation of the integrator was set at either 256 or 512 and the chart speed set at 0.25 cm/min to conserve paper. A helium gas line was connected to autosampler which pressurized the vials prior to injection and purged the sample lines after each injection.

External standards for arabinose and furfural were run before and after the reaction samples. These standards provide a relationship between the absorbance readings of the arabinose and furfural and their respective concentrations. New standards were also

prepared every three weeks and stored in a refrigerator to minimize microbial growth.

The Beckman integrator was programmed to calculate the calibration curves for pure furfural and arabinose. Once the response factors for both components are known the integrator determined the concentrations of arabinose and furfural in each sample. Over the range of arabinose and furfural concentrations in the reaction mixtures (0 to 0.1 M), the calibration curves were found to be linear. As a precautionary measure the response factors of arabinose and furfural were calculated using the regression software package, Statgraphics, and afterwards the sample concentrations determined by multiplying the peak areas by their respective response factors. The results from the Beckman integrator and the Statgraphics calculations were in good agreement with each other.

3.4 Analysis of the Solvent Phase

Analysis of furfural in the solvent (o-nitrotoluene) phase was conducted by an HP 5840A Gas Chromatograph. Two stainless steel 1/8" OD and 6 ft. long columns were used in the GC. These columns were packed with 80/100 mesh material on Hayesep Q support. The oven temperature was set at 265°C and the helium (mobile phase) flow rate was approximately 25 ml/min through the reference and sample lines. A thermal conductivity detector was used as the detection unit in the GC. Samples (3μL) were manually injected into the column port and the average retention time for the furfural peak was 2.6 min; the o-nitrotoluene peak followed at 12.0 min.

Furfural standards were run prior to the samples. The calibration plots for furfural were found to be linear, and the furfural response factors were calculated from the slope of the concentration versus time graphs. Furfural concentrations in each sample were calculated by multiplying the response factor by the furfural peak areas.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Aqueous Phase Conversion of Arabinose to Furfural

4.1.1 Dehydration of Arabinose in a Batch Reactor

The rate of the disappearance of arabinose in acidic solutions has been modeled as a first-order reaction.

$$\frac{d[A]}{dt} = -k_1[A] \qquad (4\text{-}1)$$

Equation (4-1) can be integrated analytically to give the following first-order expression,

$$[A] = [A]_0 \exp[-k_1 t] \qquad (4\text{-}2)$$

where

$[A]_0$ = initial arabinose concentration (M)

k_1 = rate constant (min^{-1})

t = time (min)

The k_1 values can be determined from the slope of the log [A] versus time plot.

Several experiments were conducted in which dilute solutions of known arabinose and sulfuric acid concentration were heated to a uniform temperature, and the decreasing concentration of arabinose measured as a function of time. Three different acid concentrations and four different reaction temperatures were used in the kinetic experiments for a total of ten different reaction conditions as indicated in Table 4-1. The acid concentrations were confirmed by titrating the samples with a standard 0.1 M NaOH solution using methyl red as the indicator. Methyl Red has a color transition range from a pH of 4.4 (red) to a pH of 6.2 (yellow). An acid range indicator was chosen to offset the carbonate error created by the solubility of carbon dioxide in water (Skoog et al., 1978).

Samples were taken at particular time intervals to give arabinose concentration-time data in the range of

$$0.10\ M > [A] > 0.01\ M$$

HPLC results of reaction samples when arabinose concentrations were less than 0.01 M were infrequently used because the arabinose peak was overshadowed by various extraneous and unidentifiable peaks.

TABLE 4-1

Reaction Conditions and Arabinose Rate Constants k_1 at Various Temperatures and Acid Concentrations

Run No.	T (°C)	$[H_2SO_4]$ (M)	$k_1(min^{-1})$
1	140	0.049	0.0090
2	140	0.095	0.0115
3	160	0.049	0.0417
4	160	0.095	0.0590
5	180	0.025	0.0920
6	180	0.049	0.164
7	180	0.095	0.215
8	200	0.025	0.345
9	200	0.049	0.483
10	200	0.095	0.921

However, arabinose and furfural concentration data were taken at longer time intervals in order to model the formation and degradation of furfural. The values of k_1 in the table were determined from the ten separate plots of log [A] vs. time. Two of these plots are shown on Figures 4-1 and 4-2. The solid line represents the equation of the line calculated from the linear regression analysis. The calculated rate constants, k_1, are tabulated according to the reaction temperature and acid concentration and displayed in Table 4-1. The concentration time profiles were corrected for the heat up times by omitting data taken at reaction times less than five minutes. The time scale was also shifted until the y-intercept of the log [A] versus time plot read 0.1 M arabinose, the initial concentration. After approximately five minutes the reaction mixture was assumed to be at the appropriate temperature and the slope of the log [A] versus time plots would yield the rate constant k_1.

The data for each plot showed a good linear fit with random scatter about the fitted regression line as the model would predict.

As discussed in Section 2.1, the proposed model for the rate constant k_1 is

$$k_1 = k_{1_0}[H_2SO_4]^a \exp[-E_1/RT] \qquad (4\text{-}3)$$

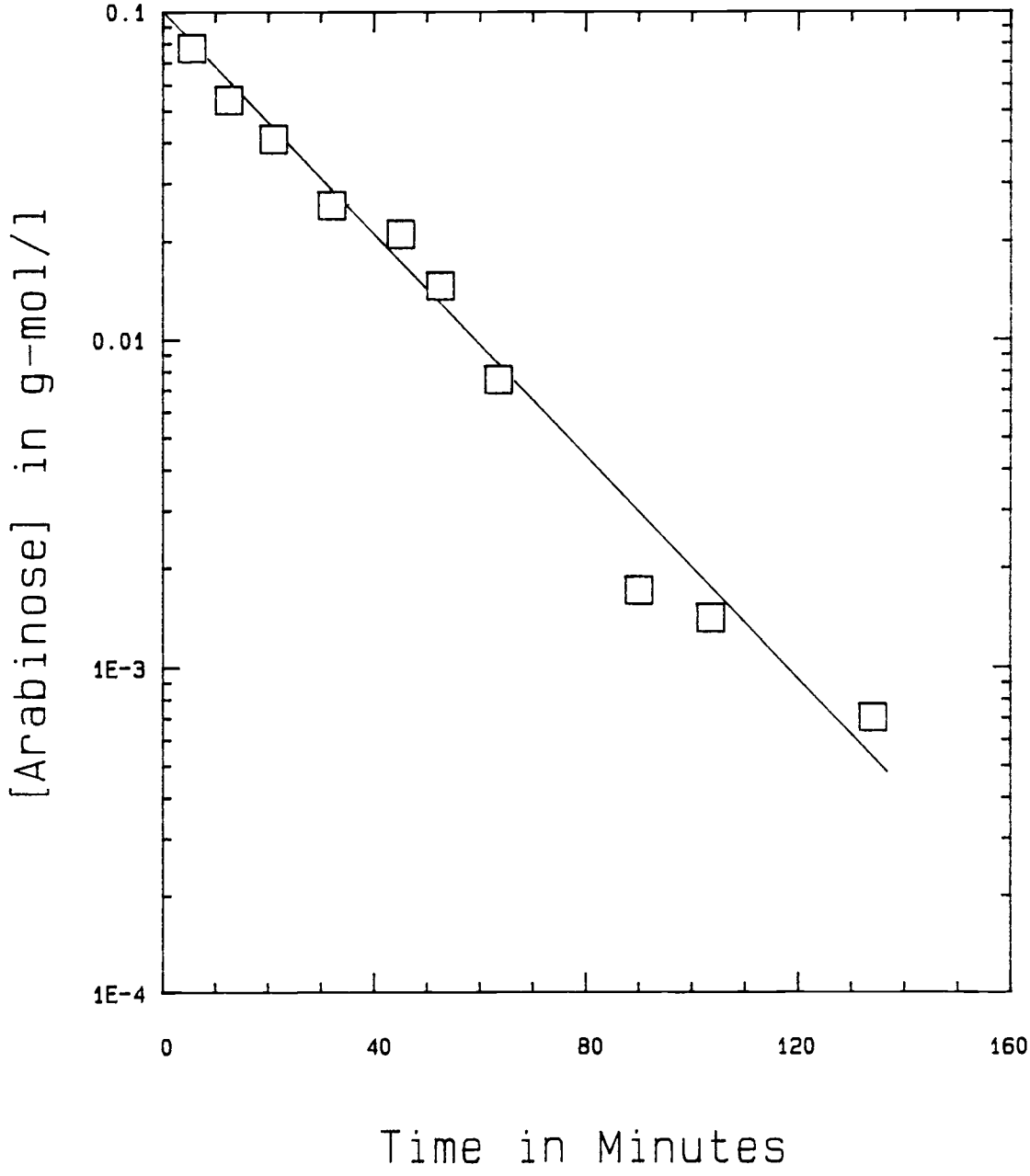

Figure 4-1

Kinetic Data for the Dehydration of Arabinose
in Dilute Sulfuric Acid
T = 160°C $[H_2SO_4]$ = 0.05 M

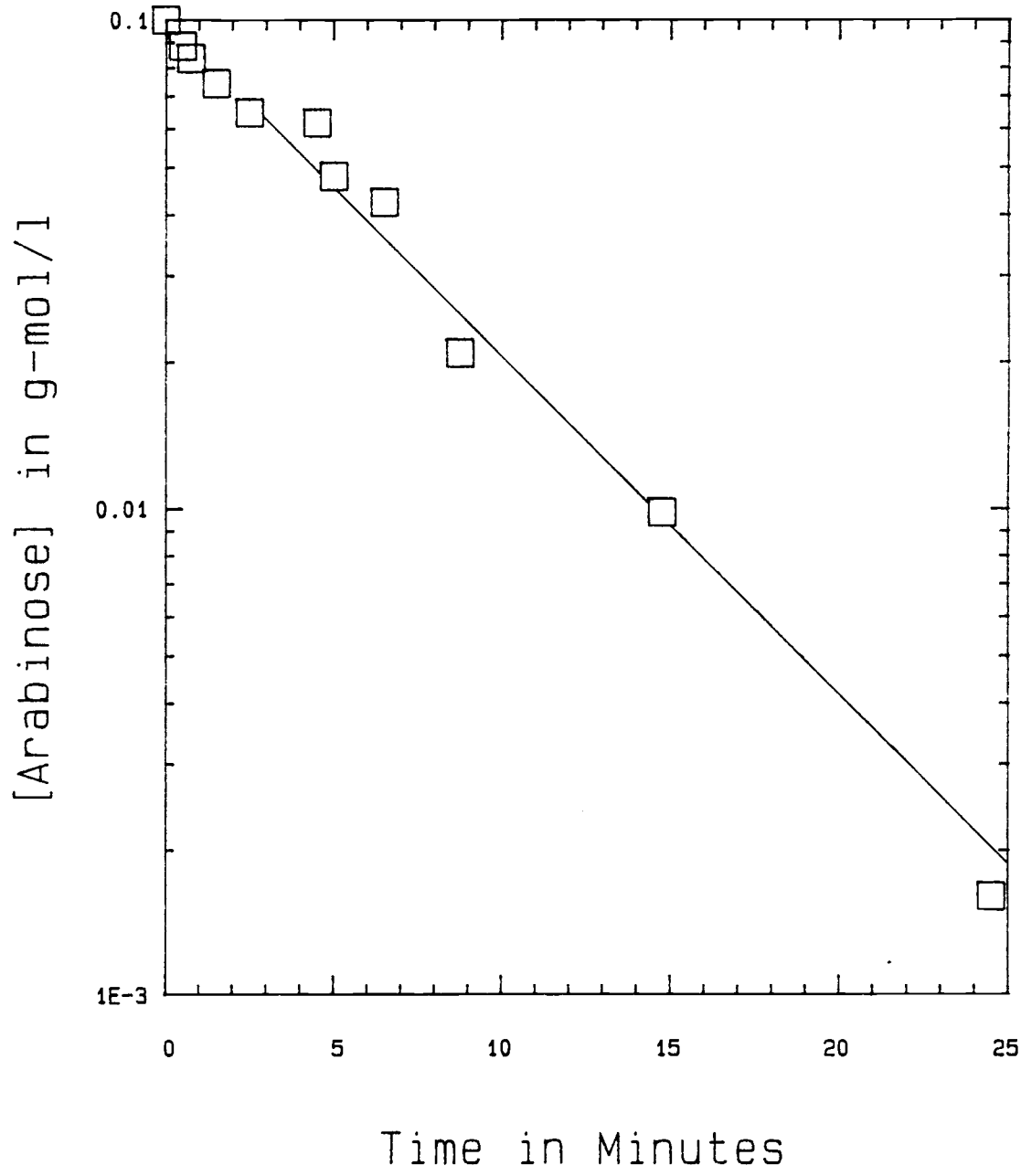

Figure 4-2

Kinetic Data for Dehydration of Arabinose
in Dilute Sulfuric Acid
T = 180°C $[H_2SO_4]$ = 0.05 M

Taking the logarithm of both sides of equation (4-3) results in equation (4-4), one can calculate the Arrhenius parameters by multiple regression.

$$\ln k_1 = \ln k_{1_0} + a \ln[H_2SO_4] - \frac{E_1}{RT} \qquad (4\text{-}4)$$

Values of the activation energy (E_1), the pre-exponential factor (k_{1_0}), and the exponential factor (a) were were calculated by multiple regression and the computed values within a 95% confidence interval were,

$$E_1 = 28300 \pm 2000 \quad \text{cal/g-mol K}$$
$$k_{1_0} = 4.74 \times 10^{13} \quad \text{min}^{-1}$$
$$a = 0.65 \pm 0.23$$

The complete Arrhenius model for the rate constant k_1 follows.

$$k_1 = (4.74 \times 10^{13})[H_2SO_4]^{0.65} \exp[\frac{-28300}{RT}] \qquad (4\text{-}5)$$

The Arrhenius expression does predict the rate constant k_1 with reasonable accuracy as shown in the plot of k_1 (observed) versus k_1(predicted) presented in Figure 4-3. The data points are scattered in a random fashion, however, the variance is larger at higher

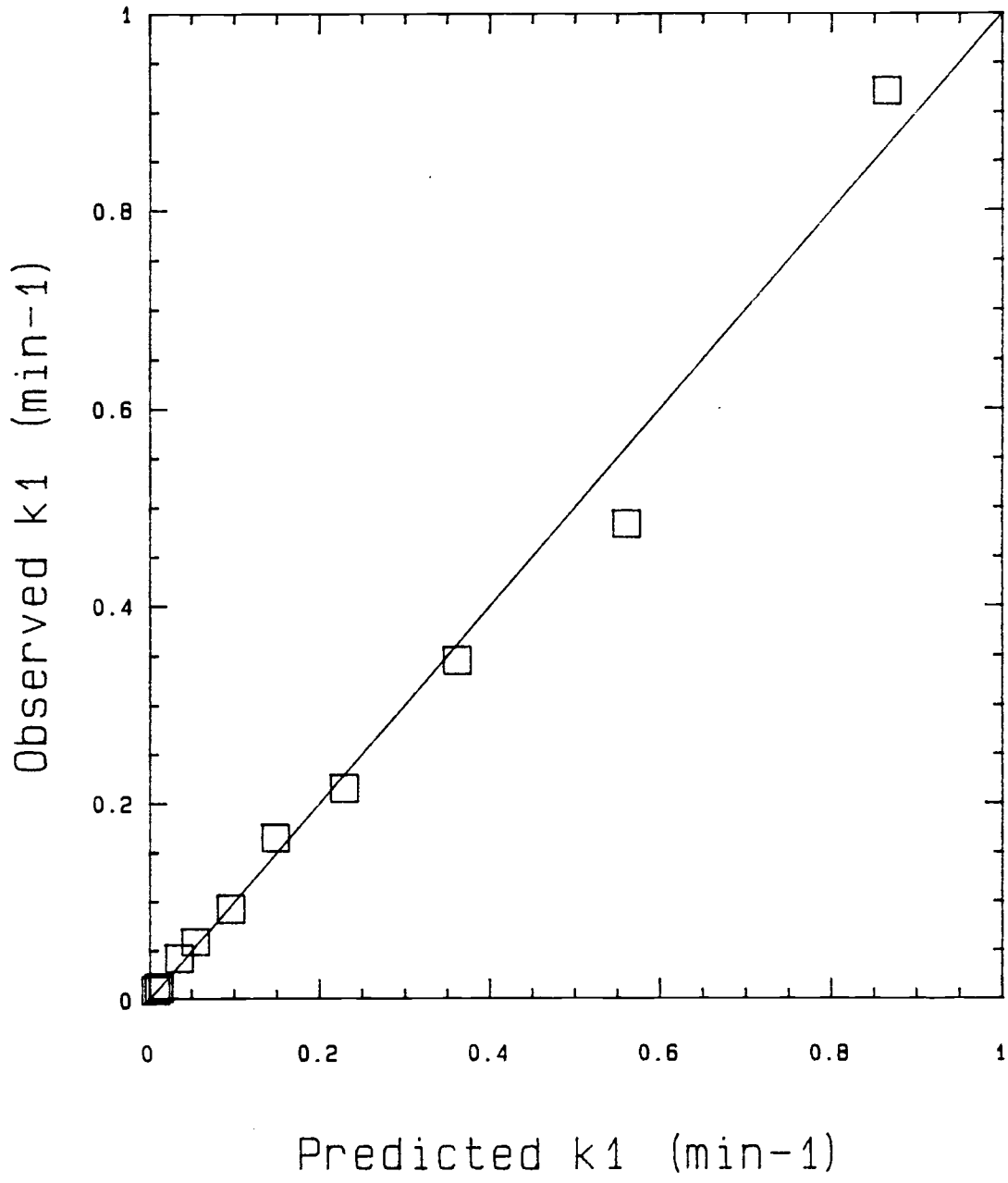

Figure 4-3

Agreement of Observed and Predicted Rate Constants
$0.025\ M \leq [H_2SO_4] \leq 0.10\ M$
$140°C \leq T \leq 200°C$

values of k_1 (high temperatures and high acid concentrations). This can be explained by the difficulties encountered at analyzing the arabinose and furfural concentrations at specific times because of the faster reaction rates. An Arrhenius plot for k_1 shown in Figure 4-4 also indicates good agreement between the model and the experimental data.

The activation energy for the degradation of arabinose was noted to be much smaller than that for the degradation of xylose. However, the pre-exponential factor for the arabinose reaction was several orders of magnitude smaller that the corresponding factor for xylose.

For arabinose:

$$E_1 = 28300 \text{ cal/g-mol K}$$
$$k_{1_0} = 4.74 \times 10^{13} \text{ min}^{-1}$$

For xylose (Sproull, 1986):

$$E_1 = 32400 \text{ cal/g-mol K}$$
$$k_{1_0} = 1.56 \times 10^{16} \text{ min}^{-1}$$

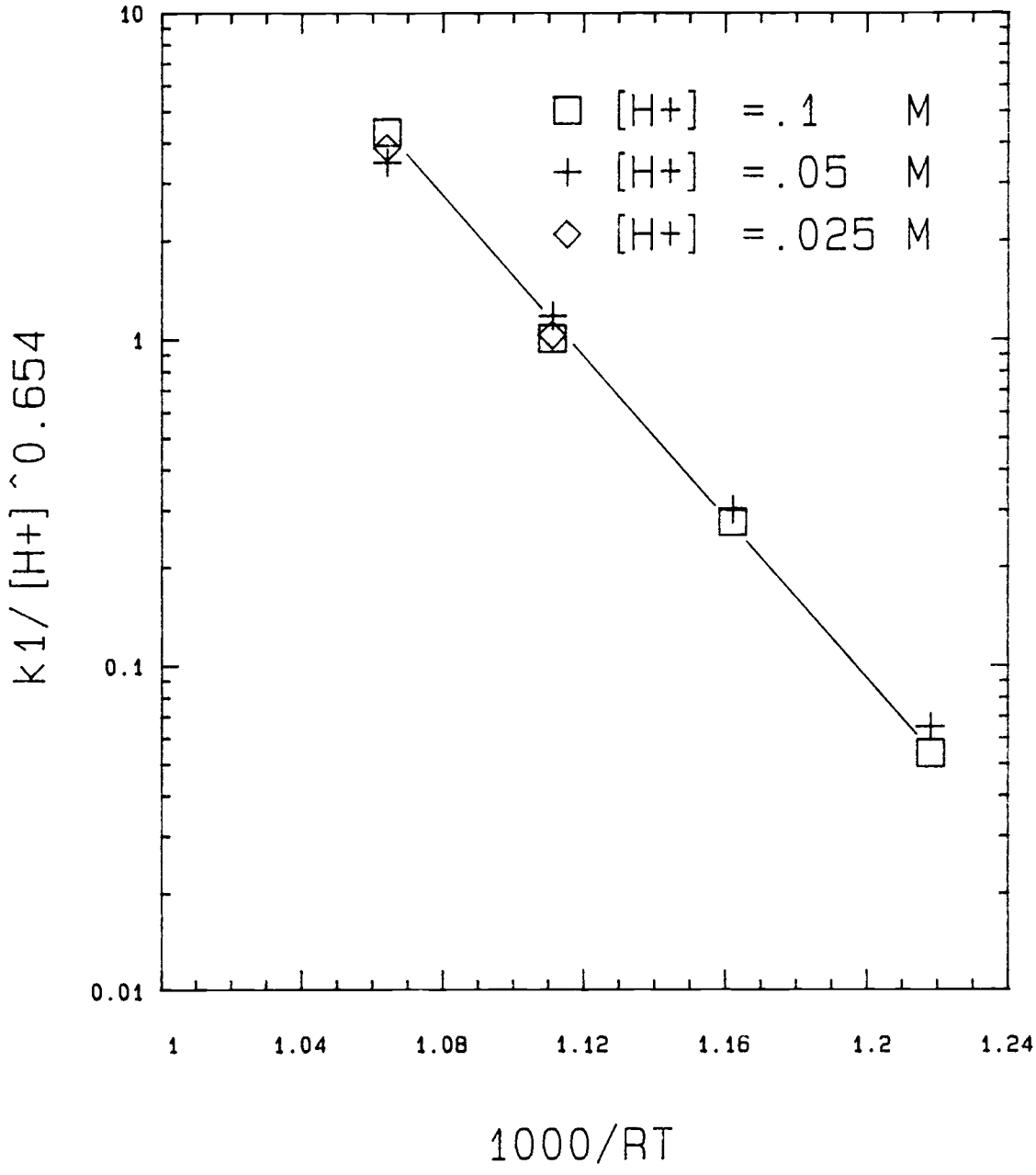

Figure 4-4

Arrhenius Plot for k_1

$140°C \leq T \leq 200°C$

$0.025\ M \leq [H_2SO_4] \leq 0.10\ M$

The differences are probably attributed to the different stereochemical properties, namely the mutarotation velocities, of each pentose.

These results suggest that k_1(arabinose) > k_1 (xylose), and that arabinose is less stable than xylose in acidic solutions.

4.1.2 Determination of the Rate Constant k_3

To determine the Arrhenius parameters k_{3_0} and E_3 the arabinose and furfural concentration-time data were utilized from all ten reaction conditions. Once again the rate constant was modeled as:

$$k_3 = k_{3_0}[H_2SO_4]^a \exp[-E_3/RT] \qquad (4\text{-}6)$$

The best estimates for k_3 were found for each data set of furfural concentration versus time. A computer program was written which varied the value of k_3 and integrated the furfural rate expression,

$$r_F = \frac{d[F]}{dt} = k_1[A] - k_2[F] - k_3[A][F] \qquad (4\text{-}7)$$

over the total reaction time. This program utilized a Fourth Order Runge-Kutta subroutine to perform the numerical integration (Appendix I). The value of k_3 was determined for each data set which minimized the sum of squares of error terms for observed and predicted furfural concentrations.

$$SSE = ([F]_{ob} - [F]_t)^2$$

where,

$[F]_{ob}$ = observed furfural concentration (M)

$[F]_t$ = predicted furfural concentration (M)

By taking the logarithm of both sides of equation (4-6) allows one to calculate the Arrhenius parameters by multiple regression.

$$\ln k_3 = \ln k_{3_0} + a \ln [H_2SO_4] - \frac{E_3}{RT} \qquad (4\text{-}8)$$

Within a 95% confidence the results were as follows,

$E_3 = 25000 \pm 2000$ cal/g-mol K

$k_{3_0} = 2.16 \times 10^{13}$ min^{-1} M^{-1}

$a = 0.52 \pm 0.14$

The rate constant k_2 has been determined in previous work (Sproull, 1986) and these results were used in the proposed 3-constant model for the conversion of arabinose to furfural.

$E_2 = 22070$ cal/g-mol K

$k_{2_0} = 2.83 \times 10^9$ min^{-1}

$a = 1.00$

The fact that $E_1 > E_2$ suggests that a higher reaction temperature will result in a higher furfural yield. This

result was shown experimentally for the dehydration of xylose to furfural (Root et al, 1959).

Combining the three rate constants, k_1, k_2, and k_3 into the Dunlop model, the predicted and observed arabinose and furfural concentration-time profiles were plotted for the temperature range of 140°C to 200°C and acid concentrations between 0.025 M and 0.10 M. Figures 4-5 and 4-6 are two representative plots. These figures show that the model overestimates the furfural concentrations at early times but accurately represents the furfural concentration after the maximum is reached. Errors are probably attributed to the simplified reaction mechanism for the conversion of arabinose to furfural, since all reaction intermediates are treated as a single species.

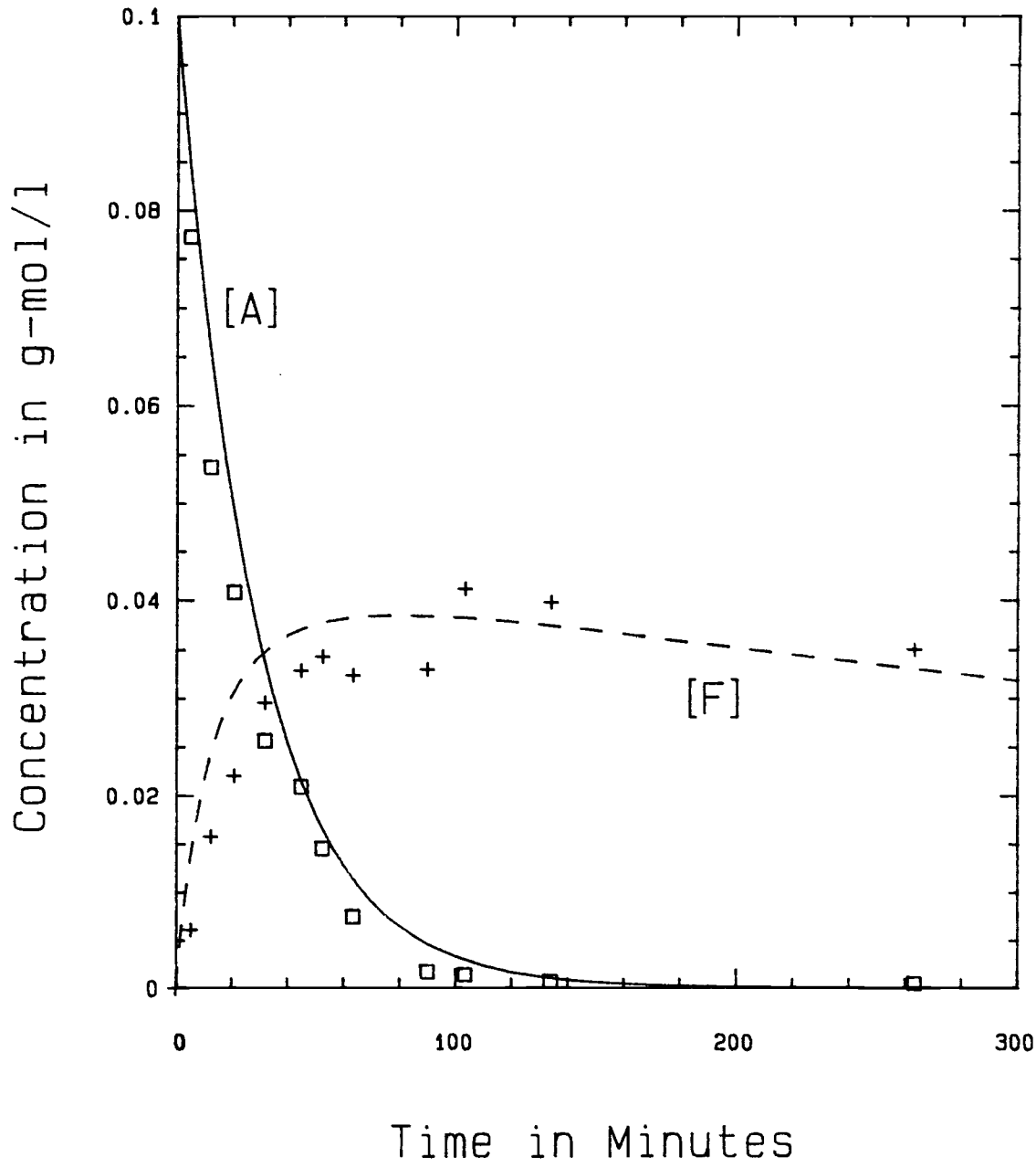

Figure 4-5

Comparison of Predicted and Observed
Concentration Profiles in the Aqueous Phase
T = 160°C $[H_2SO_4]$ = 0.05 M $[A]_0$ = 0.10 M

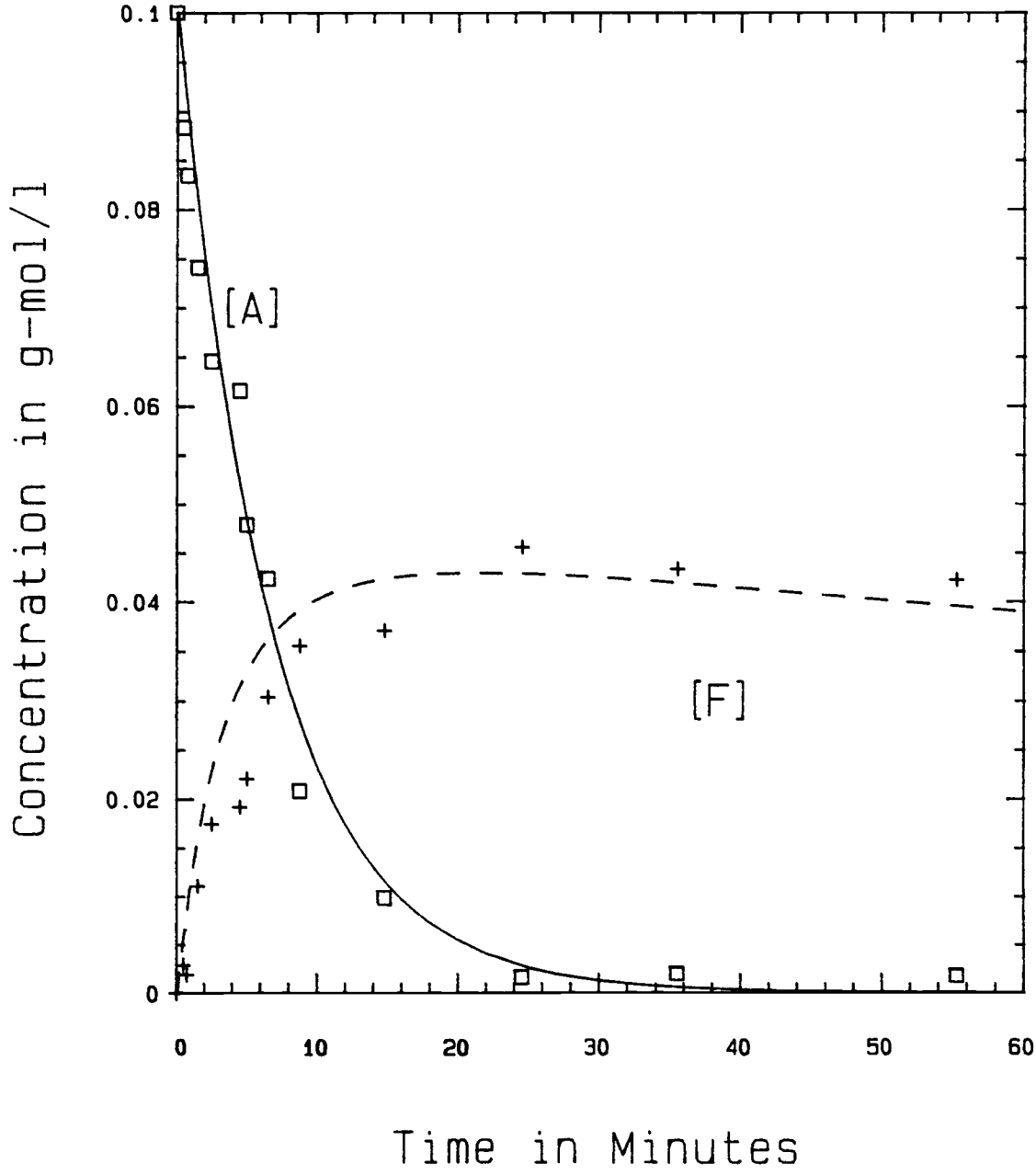

Figure 4-6

Comparison of Observed and Predicted Concentration Profiles in the Aqueous Phase
T = 180°C $[H_2SO_4]$ = 0.05 M $[A]_0$ = 0.10 M

4.2 Two-Phase Kinetics

Furfural does not degrade appreciably in the solvent (o-nitrotoluene) phase but does degrade in the acidified aqueous phase. Therefore, to reduce the degradation of furfural, the furfural should be extracted into the solvent phase as soon as it is formed. Whether the process is reaction or diffusion controlling can be determined experimentally. However, one must assume that the aqueous phase kinetics are unaffected by the presence of the solvent.

Two-phase experiments were performed at three different acid concentrations, 0.025 M, 0.05 M, and 0.1 M and at the respective reaction temperatures 200°C, 180°C and 160°C. Some of the results appear as Figures 4-7 and 4-8. Since the two phase mixtures were analyzed at room temperature, solvent and aqueous furfural concentrations were corrected to represent the values at the reaction temperature. For these calculations equation (4-9), the relationship for the furfural distribution coefficient as a function of temperature, was applied (Sproull, 1986).

$$m = 5.71\exp[335/RT] \qquad (4\text{-}9)$$

where the following variables are defined:

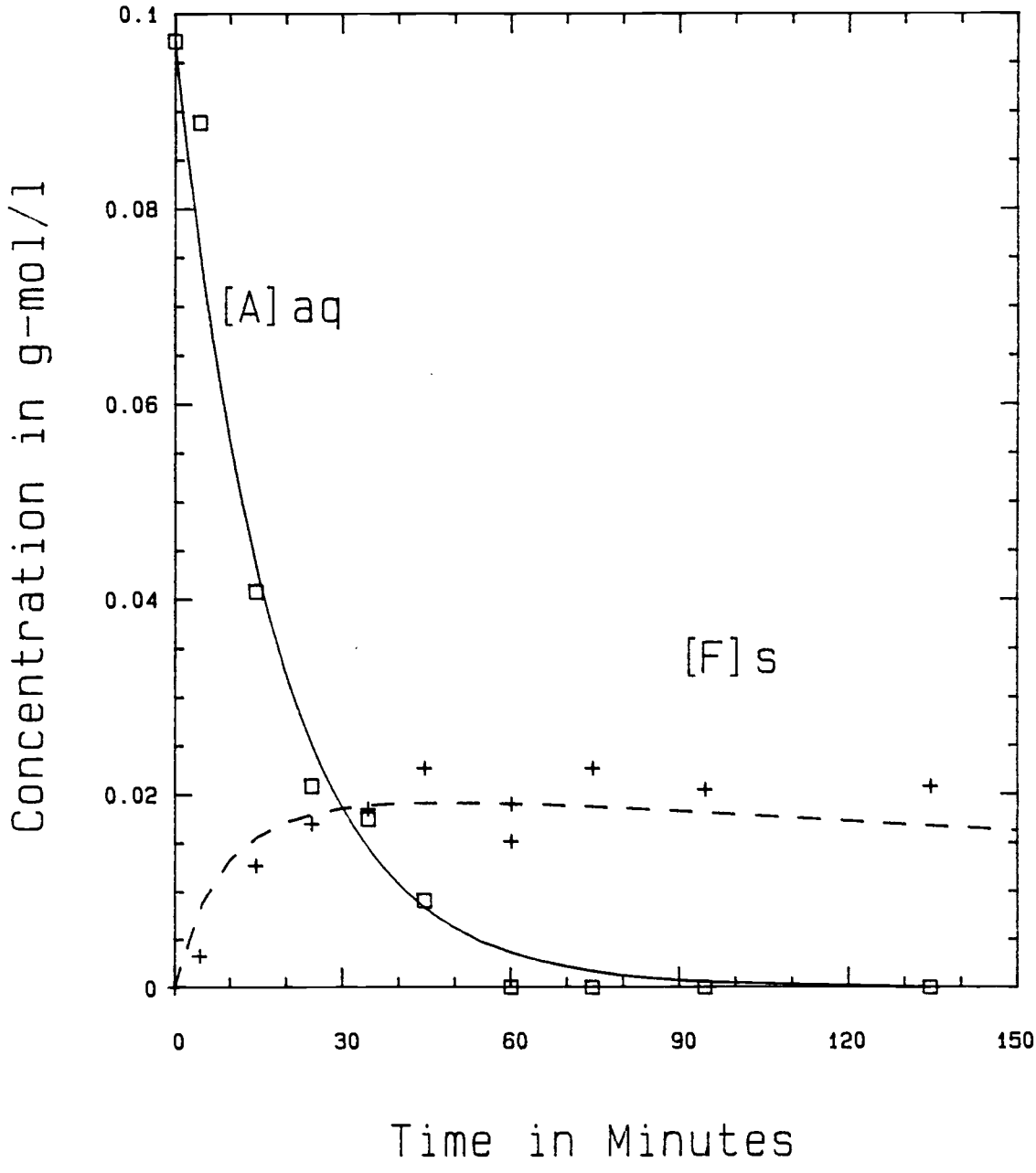

Figure 4-7

Predicted and Observed Concentration Profiles
in a Two-Phase Batch Reactor
$T = 160°C$ $[H_2SO_4] = 0.10$ M $\Phi = 2.0$
$[A]_0 = 0.10$ M $[F]_{s_0} = 0.0$ M

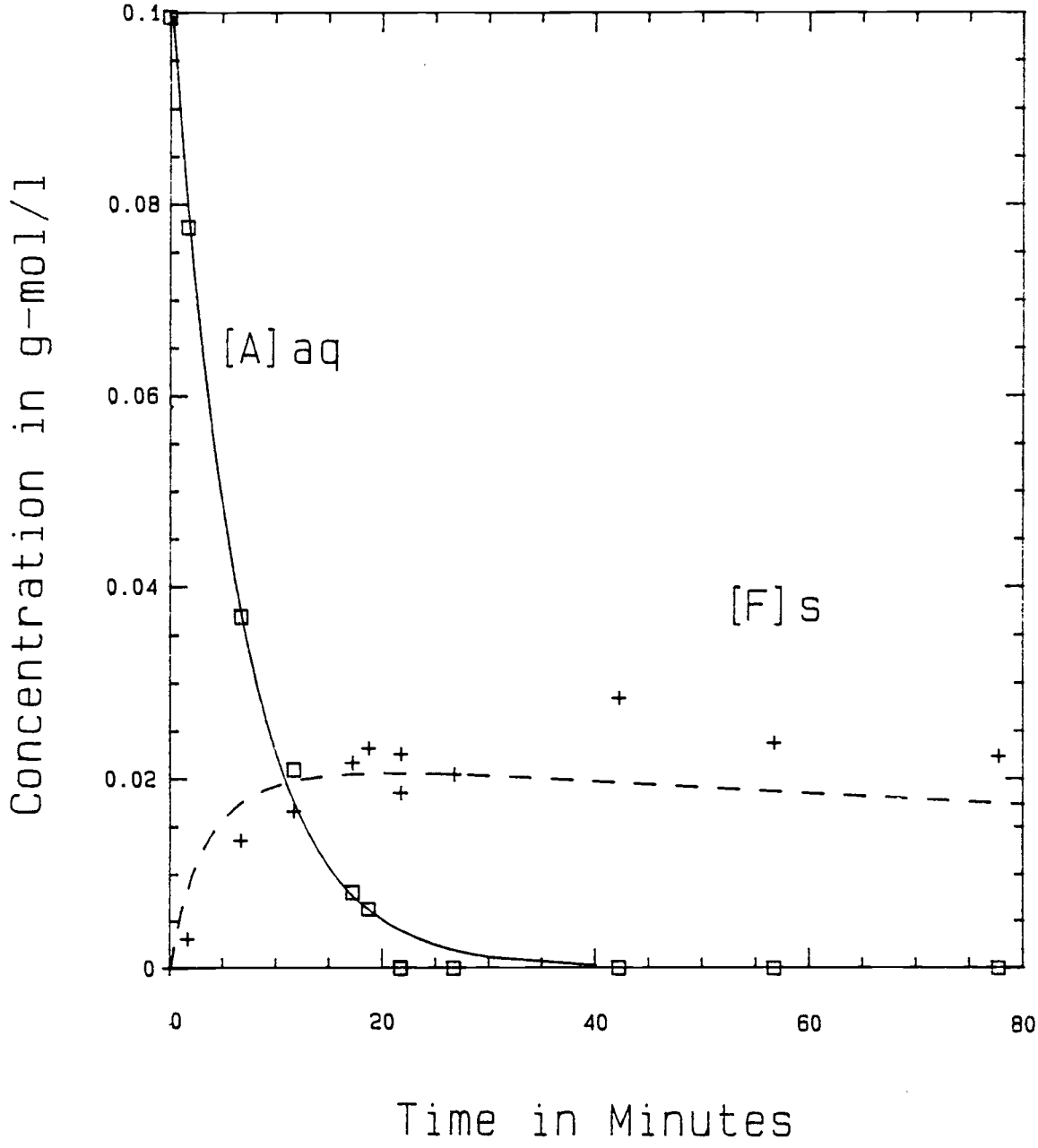

Figure 4-8

Predicted and Observed Concentration Profiles
in a Two Phase Batch Reactor
T = 180°C $[H_2SO_4]$ = 0.05 M Φ = 2.0
$[A]_0$ = 0.10 M $[F]_{s_0}$ = 0.0 M

$$m = \frac{[F]s}{[F]aq}$$

R = 1.987 cal/g-mol K

T = temperature (K)

Since the two phase reaction mixtures were not agitated, and realizing the small cross-sectional area of the reaction bombs, it was reasonable to assume this process was diffusion-controlled. In addition, a resinous material collected at the water-solvent interface which would retard the diffusion of furfural from the aqueous phase to the solvent phase.

To check the validity of equation (4-9), the distribution coefficients were evaluated from the experimental data by HPLC and GC analysis of the aqueous and solvent phases respectively. At room temperature (19°C), the theoretical distribution coefficient as calculated by equation (4-9) is 10.2. The experimentally calculated distribution coefficients were in good agreement with this value.

The theoretical furfural concentration profiles fit the experimental data at early reaction times, in particular at reaction times leading up to the maximum furfural concentration. At longer times the theoretical furfural concentrations were lower than the experimental values. The discrepancy is probably due to the assumption

that the process is diffusion-limiting. While the degradation of arabinose occurs in the aqueous phase, a small fraction of furfural is protected as it diffuses into the solvent phase. When the concentration of furfural in the aqueous phase is small, mass transfer must occur in the opposite direction before degradation can occur in the aqueous phase. This would result in higher observed furfural concentrations in both phases, than predicted by the diffusion-limited model. However, the model needs only to provide an accurate estimation of the furfural concentration up through the optimum residence time, where the furfural concentration is a maximum. This would be the information used to design the two-phase reactor for furfural production.

To increase the overall furfural yield, the two-phase system needs agitation to increase both the interfacial area and mass transfer of furfural into the solvent phase. In the limiting case, for instantaneous mass transfer, the furfural yield will nearly double (Figure 4-9).

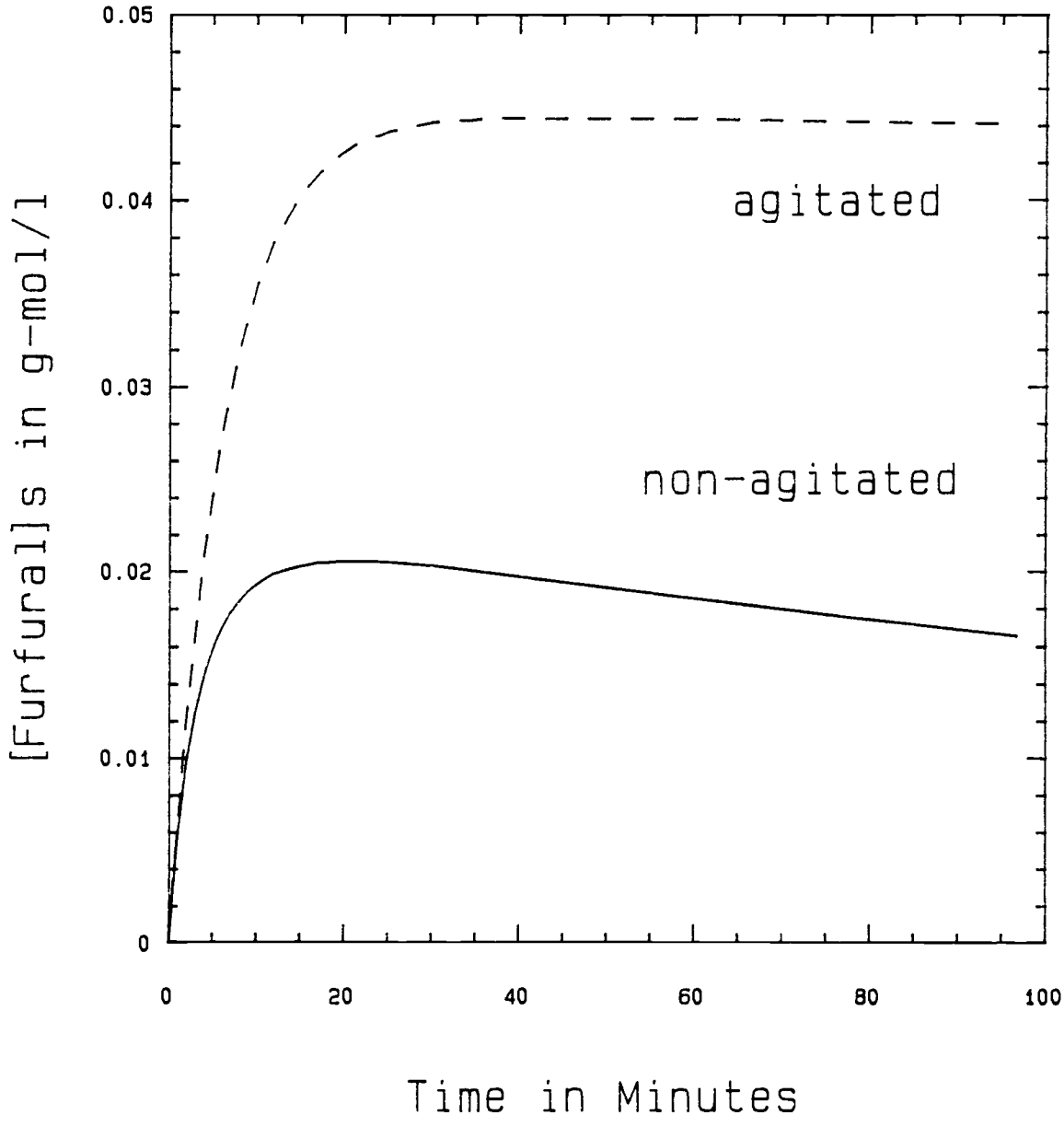

Figure 4-9

Predicted Solvent Phase Concentration Profiles for Agitated and Non-Agitated Two Phase Batch Reactor

$T = 180°C \quad [H_2SO_4] = 0.05\ M \quad \Phi = 2.0$

$[A]_0 = 0.10\ M \quad [F]_{s_0} = 0.0\ M$

4.3 Furfural Degradation in o-Nitrotoluene

Since furfural was extracted in an o-nitrotoluene solvent phase it must be determined if degradation of the former occurs in the solvent phase at the reaction temperature. One must also assume that sulfuric acid is insoluble in the o-nitrotoluene so that acid catalyzed degradation of furfural does not occur. This assumption is reasonable since a highly polar substance is unlikely to be miscible in a non-polar solvent.

Samples (9.3 ml) of 0.11 M furfural (in o-nitrotoluene) were heated in the reaction vessels for specified time intervals up to two hours. The experiments were repeated at two temperatures, 180°C and 200°C. The furfural from a specified volume of the solvent phase mixture was extracted by a known volume of distilled water and the aqueous phase was analyzed for furfural content in the HPLC system. Since the distribution coefficient was known, the original furfural concentration in the solvent phase was calculated. The results appear on Figures 4-10 and 4-11. These plots show that furfural degradation in o-nitrotoluene was negligible. The implications of this are important because the rational for extracting the furfural in the o-nitrotoluene phase is to reduce the amount degraded in the aqueous phase.

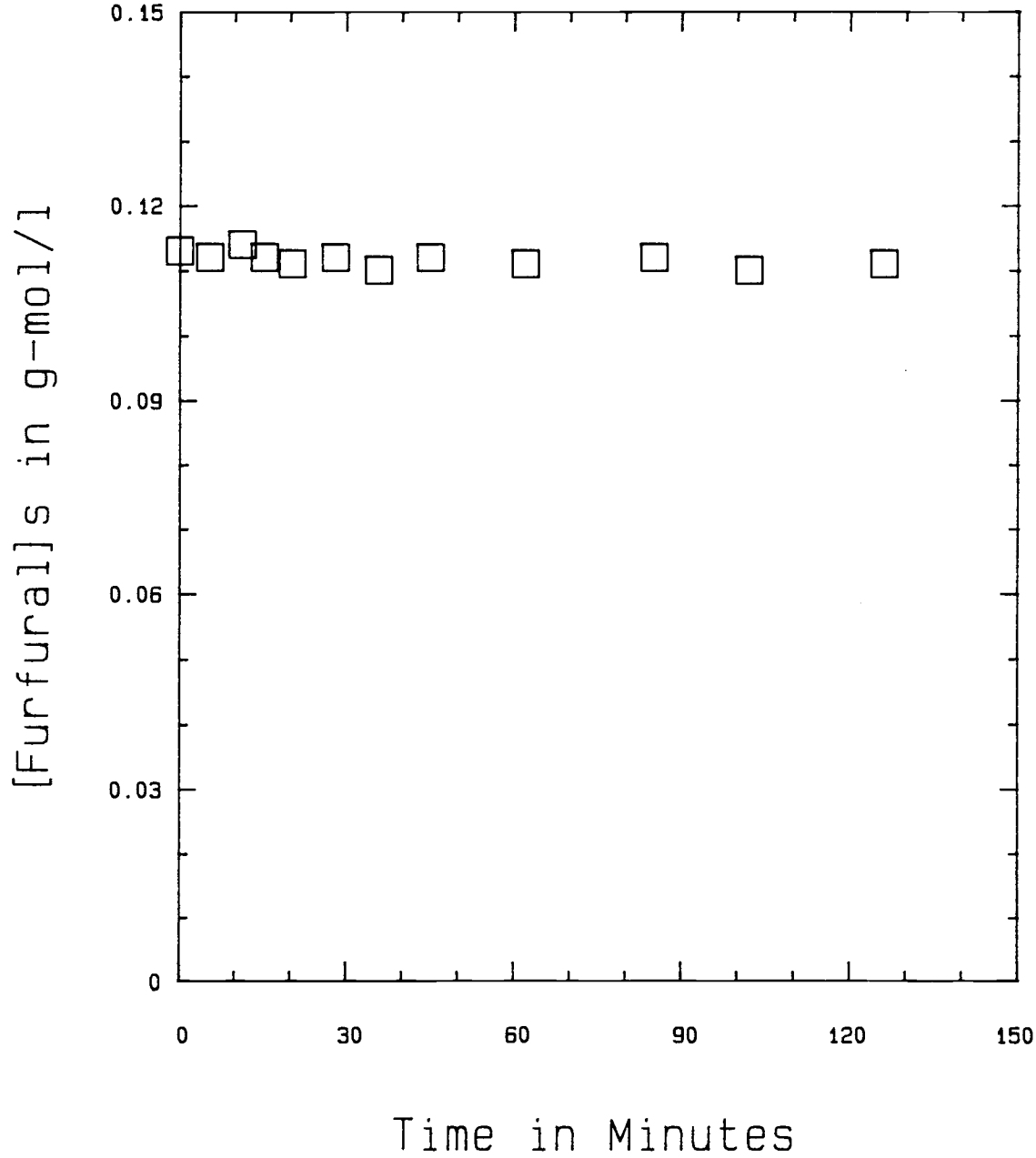

Figure 4-10

Solvent Phase Concentration Profile to Determine the Extent of Furfural Degradation in o-Nitrotoluene
T = 180°C $[F]_{s_0}$ = 0.11 M

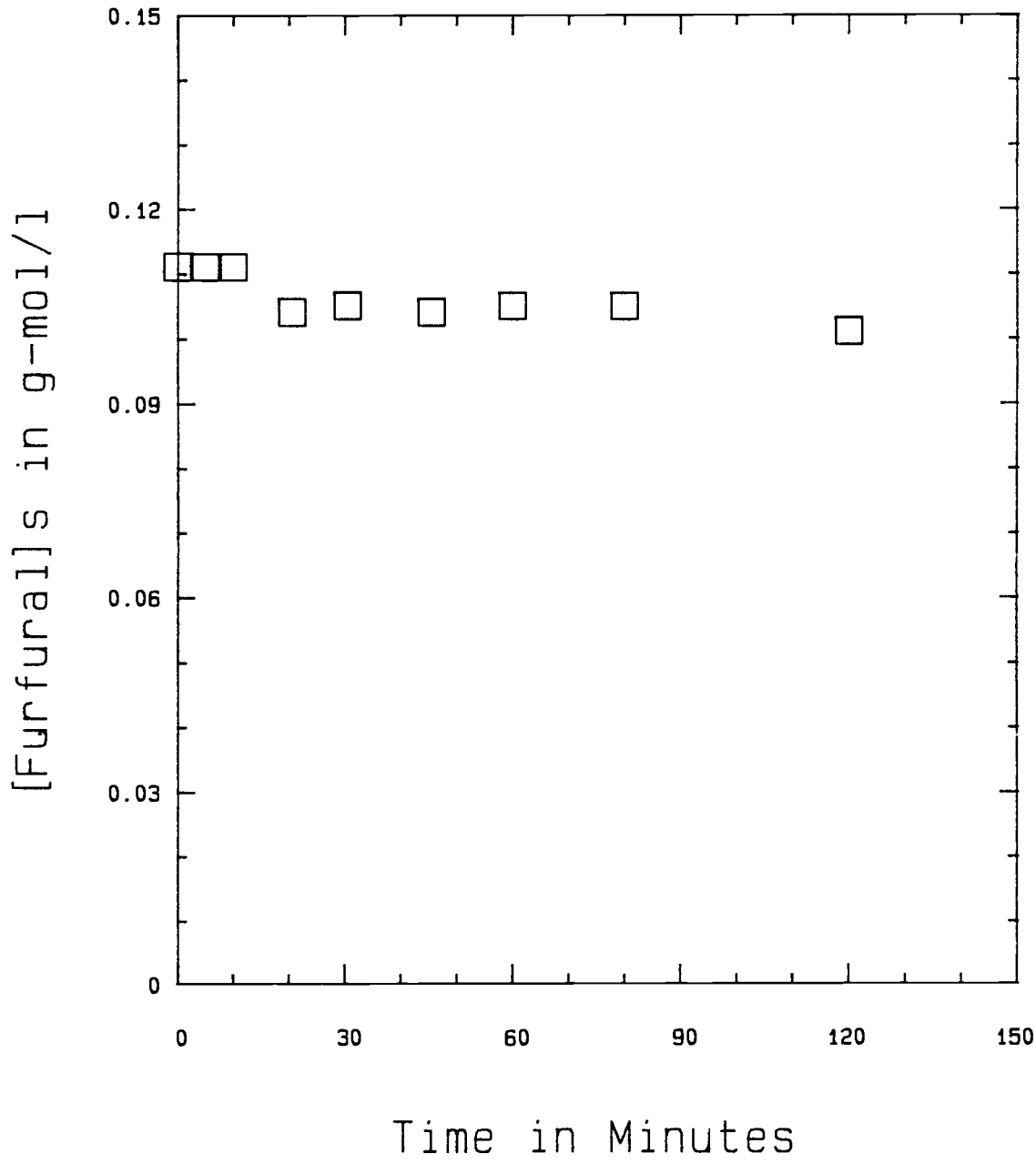

Figure 4-11

Solvent Phase Concentration Profile to Determine the Extent of Furfural Degradation in o-Nitrotoluene
T = 200°C $[F]_{s_0}$ = 0.11 M

CHAPTER 5

SUMMARY AND CONCLUSION

5.1 Aqueous Phase Kinetics

The proposed three-constant model accurately predicts the arabinose and furfural concentration profiles, for sulfuric acid concentrations between 0.025 and 0.1 M and for the reaction temperature range of 140°C to 200°C. It has also been shown that the rate constants k_1 and k_3 can be modeled by an Arrhenius expression.

$$k_i = k_{i_0}[H_2SO_4]^a \exp[E/RT] \qquad (5\text{-}1)$$

For arabinose, the exponent ,'a', was found to be 0.65, whereas the work performed with xylose (Root et al., 1959; Sproull, 1986) indicated that the exponent was unity.

5.2 Two Phase Kinetics

The two phase kinetic experiments revealed several things.

(1) Without agitating the two phases and with the small interfacial area of the reaction vessels, the process could be assumed to be diffusion-controlled.

(2) The aqueous phase kinetic model is unaffected by the presence of o-nitrotoluene, and could be used in conjunction with the furfural distribution coefficient to give estimated furfural concentrations in both aqueous and solvent phases.

(3) To increase the furfural yield, one needs to agitate the two liquid phases during the reaction.

CHAPTER 6

RECOMMENDATIONS FOR FUTURE WORK

(1) A two phase reactor designed for the production of furfural will require an agitation system to increase the mass transfer of furfural into the solvent phase. Therefore, studies should be conducted to examine the improved furfural yield with an agitated two-phase system.

(2) Xylose and arabinose are the primary pentoses found in hemicellulose, which yield furfural by acid degradation. It would seem that acid degradation experiments should be conducted with both components present to determine if interaction terms exist between them.

(3) To increase the resolution of peaks in carbohydrate solutions, an effort should be made to investigate the performance of the HPLC lead(II) resin column, one used by many research workers in the field of carbohydrate chemistry.

BIBLIOGRAPHY

Angyal, S.J.: Sugar-Cation Complexes-Structure and Applications, J. Chem. Soc. Review, 9(4): 415 (1980).

Borchardt, L.G. and C.V. Piper: A Gas Chromatographic Method for Carbohydrates as Alditol-Acetates, TAPPI, 53(2): 257 (1970).

Bott, H.G. and E.L. Hirst: Formation of Furfural from Methylated Pentoses, J. Chem. Soc., 1932: 2621.

Brower, H.E., J.E. Jeffery and M.W. Folsom: Gas Chromatographic Sugar Analysis in Hydrolyzates of Wood Constituents, Anal. Chem., 38(2): 363 (1966).

Dean, J.A., Ed.: Lange's Handbook of Chemistry, 13th ed., McGraw-Hill, New York (1985).

Dunlop, A.P. : Furfural Formation and Behavior, Ind. Eng. Chem., 40(2): 204 (1948).

Dunlop, A.P. and F.N. Peters Jr.: The Furans, Reinhold Publishing Corp., New York, (1953).

Dunlop, A.P. and F.N. Peters Jr.: Thermal Stability of Furfural, Ind. Eng. Chem., 32(12): 1639 (1940).

Dunlop, A.P., P.R. Stout, and S. Swadesh: Autoxidation of Furfural, Ind. Eng. Chem., 38(7): 605 (1946).

Goldstein, I.S.: Organic Chemicals From Biomass, CRC Press, Inc., Boca Raton, Florida (1981).

Harris, J.F.: Process Alternatives for Furfural Production, TAPPI, 61(1): 41 (1978).

Harris, J.F.: Two Stage, Dilute Sulfuric Acid Hydrolysis of Wood: An Investigation of Fundamentals, U.S. Dept. of Agriculture (1985).

Harris, J.F. and J.M. Smuk: Economics of the Production of Furfural From Xylose Solutions, For. Prod. Jour., 11: 303 (1961).

Hughes, E.E. and S.F. Acree: Quantitative Formation of Furfural From Xylose, J. Res. Natl. Bur. Stand., 21: 327 (1938).

Hurd, C.D. and L.L. Isenhour: Pentose Reactions I. Furfural Formation, J. Am. Chem. Soc., 54: 317 (1932).

Kemp, L.C., G.B. Hamilton and H.H. Gross: Furfural as a Selective Solvent in Petroleum Refining, Ind. Eng. Chem., 40(2): 220 (1948).

Lazera, Manuel, Jose' Martinez-Benet, and Lius Prigjaner: Plant Design and Optimization for the Production of Furfural from Xylose Solutions, Ind. Eng. Chem., 40(2): 687 (1986).

Morita, H. and W.G. Montgomery: Gas Chromatography of Silylated Oxime Derivatives of Peat Monosaccharides, J. Chromatogr., 155: 195 (1978).

Paice, M.G., L. Jurasek and M. Desrochers: Simplified Analysis of Wood Sugars, TAPPI, 65(7): 103 (1982).

Palmer, J.K.: A Versatile System for Sugar Analysis via Liquid Chromatography, Anal. Lett., 8(3): 215 (1985).

Panicker, P.K.N.: Furfural, Chemical Age of India, 25(11): 793 (1975), 26(2): 101 (1975), 26(6): 457 (1976).

Patel, A.N.: Ternary Phase Equilibrium Studies of Furfural-Water-Solvent Systems, J. Chem. Tech. Biotechnol., 34(a): 161 (1984).

Pervier, N.C. and R.A. Gortner: The Estimation of Pentoses and Pentosans, Ind. Eng. Chem., 15(11): 1167 (1923).

Pettersen, R.C., V.H. Schwandt and M.J. Effland: An Analysis of the Wood Sugar Assay Using HPLC: A Comparison with Paper Chromatography, J. Chromatogr. Sci., 22(11): 478 (1984).

Pillai, K.S. and P.K.N. Panicker: Pilot Plant Studies on Manufacture of Furfural from Cane Bagasse, Chemical Age of India, 30(8) (1979).

Root, D.F., J.F. Saeman and J.F. Harris: Kinetics of the Acid Catalyzed Conversion of Xylose to Furfural, For. Prod. Jour., 29: 158 (1959).

Saeman, J.F.: Kinetics of Wood Saccharification: Hydrolysis of Cellulose and Decomposition of Sugars in Dilute Acid at High Temperatures, Ind. Eng. Chem., 37(1): 43 (1945).

Sinner, M. and J. Puls: Non-Corrosive Dye Reagents for Detection of Reducing Sugars in Borate Complex Ion -Exchange Chromatography, J. Chromatogr., 156: 197 (1978).

Skoog, D.A. and D.M. West, Analytical Chemistry, 3rd ed., Holt, Rinehart and Winston Co., San Francisco, (1978).

Sproull, R.D., P.R. Bienkowski, and G.T. Tsao: Production of Furfural from Corn Stover Hemicellulose, Biotechnol. Bioeng. Symp., 15: 561 (1985).

Wentz, F.J.: The Chemical Techology of Wood, Academic Press, New York (1970).

Wentz, F.E., A.D. Marcy, and M.J. Gray: Analysis of Wood Sugars in Pulp and Paper Industry Samples by HPLC, J. Chromatogr. Sci., 20: 349 (1982).

Williams, D.L. and A.P. Dunlop: Kinetics of Furfural Destruction In Acidic Aqueous Media, Ind. Eng. Chem., 40(2): 239 (1948).

APPENDIX

Appendix I

This computer program was originally written by R.D. Sproull (1986) and was revised by Dean Yasuda to calculate an optimum value for the rate constant for k_3, for specific reaction conditions (temperature, acid concentration). The algorithm utilizes a fourth order Runge-Kutta Subroutine to perform the numerical integrations.

```
PROGRAM K3
EXTERNAL DERIV
DIMENSION C(2),DC(2)
REAL MF,K(3)
CHARACTER*64 FNAME
COMMON/KINCON/MF,K,PHI
WRITE (*,*) 'ENTER TEMPERATURE (C)'
READ (*,*) TC
WRITE(*,*) 'ENTER H+ CONCENTRATION'
READ(*,*) ACID
WRITE(*,*) 'ENTER TIME OF REACTION IN MINUTES'
READ(*,*) TMAX
WRITE(*,*) 'ENTER INITIAL ARABINOSE CONC. (M)'
READ(*,*) X0
WRITE(*,*) 'ENTER THE MEASURED VALUE OF K1'
READ(*,*) K(1)
WRITE(*,*) 'ENTER INITIAL FURFURAL AQ CONC (M)'
READ(*,*) FA0
WRITE(*,*) '                                    '
WRITE(*,*) '                                    '
WRITE(*,*) '                                    '
WRITE(*,*) 'PROGRAM TO ESTIMATE THE KINETIC'
WRITE(*,*) 'CONSTANT K3 FOR THE REACTION'
WRITE(*,*) '                                '
WRITE(*,*) 'ARABINOSE -----> FURFURAL    '
WRITE(*,*) '                                    '
WRITE(*,*) '                                    '
   CALL RATE(TC,ACID)
   WRITE(*,4) TC
   WRITE(*,8) ACID
   WRITE(*,10) TMAX
   STEP = TMAX/240
   WRITE(*,11) STEP
   WRITE(*,15) K(1)
   WRITE(*,17) K(2)
   WRITE (*,*) 'K(3) MIN-1      SSE'
   DO 1000 IK3 = 1775,1850,1
```

```
                T = 0.0
                FA = 0.0
                SSE = 0.0
                K(3) = IK3
                K(3) = K(3)/1000
                C(1) = X0
                C(2) = FA0
                DT = TMAX/240
                T = 0.0
C
C
C
C
C               ---------------------------------------
C               Optimization Section of the Program which
C               Minimizes the Sum of the Square of Errors
C               of the Observed and Theoretical Furfural
C               Concentration.
C               ---------------------------------------
C
C
C
C
C
          DO 200 J = 1,240
               CALL RUNGE(DERIV,2,T,C,DC,DT)
               X = C(1)
               FA = C(2)
                IF (T .NE. 2.5) THEN
                   GOTO 100
                ELSE
                   SSE = (0.0011 - FA)**2
                   GOTO 200
                ENDIF
 100            IF (T .NE. 4.5) THEN
                   GOTO 101
                ELSE
                   SSE = SSE + (0.0099 - FA)**2
                   GOTO 200
                ENDIF
 101            IF (T .NE. 6.5) THEN
                   GOTO 102
                ELSE
                   SSE = SSE + (0.0152 - FA)**2
                   GOTO 200
                ENDIF
 102            IF (T .NE. 9.5) THEN
                   GOTO 103
                ELSE
                   SSE = SSE + (0.0246 - FA)**2
                   GOTO 200
                ENDIF
 103            IF (T .NE. 12.5) THEN
                   GOTO 104
                ELSE
```

```
                  SSE = SSE + (0.0304 - FA)**2
                  GOTO 200
               ENDIF
104            IF (T .NE. 16.5) THEN
                  GOTO  105
               ELSE
                  SSE = SSE + (0.0383 - FA)**2
                  GOTO 200
               ENDIF
105            IF (T .NE. 19.0) THEN
                  GOTO 106
               ELSE
                  SSE = SSE + (0.0404 - FA)**2
                  GOTO 200
               ENDIF
106            IF (T .NE. 20.5) THEN
                  GOTO 107
               ELSE
                  SSE = SSE + (0.0407 - FA)**2
                  GOTO 200
               ENDIF
107            IF (T .NE. 24.5) THEN
                  GOTO 108
               ELSE
                  SSE = SSE + (0.0434 - FA)**2
                  GOTO 200
               ENDIF
108            IF ( T .NE. 32.5) THEN
                  GOTO 109
               ELSE
                  SSE = SSE + (0.0444 - FA)**2
                  GOTO 200
               ENDIF
109            IF (T .NE. 38.5) THEN
                  GOTO 110
               ELSE
                  SSE = SSE + (0.047 - FA)**2
                  GOTO 200
               ENDIF
110            IF (T .NE. 49.0) THEN
                  GOTO 111
               ELSE
                  SSE = SSE + (0.0444 - FA)**2
                  GOTO 200
               ENDIF
111            IF (T .NE. 60.0) THEN
                  GOTO 112
               ELSE
                  SSE = SSE + (0.045 - FA)**2
                  GOTO 200
               ENDIF
112            IF (T .NE. 70.0) THEN
                  GOTO 113
```

```
                ELSE
                   SSE = SSE + (0.0446 - FA)**2
                   GOTO 200
                ENDIF
 113            IF (T .NE. 85.0) THEN
                   GOTO 114
                ELSE
                   SSE = SSE + (0.0445 - FA)**2
                   GOTO 200
                ENDIF
 114            IF (T .NE. 100.0) THEN
                   GOTO 200
                ELSE
                   SSE = SSE + (0.0433 - FA)**2
                   GOTO 200
                ENDIF
 200            CONTINUE
C
C
C
C
C
C               ------------------------------------------
                Print the Sum of the Square of Errors for
                Each value of K3 Guessed.
C               ------------------------------------------
C
C
C
C
C
C
                WRITE(*,20) K(3),SSE
 1000           CONTINUE
C
C
C
C
C
C
C
C
C
   4            FORMAT(1X,'TEMP(C) = ',F7.3)
   8            FORMAT(1X,'H+ CONC = ',F9.5)
  10            FORMAT(1X,'INTEGRATION LIMIT = ',F9.5)
  11            FORMAT(1X,'STEP SIZE = ',F9.5)
  13            FORMAT(1X,3(F9.5,3X))
  15            FORMAT(1X,'k1 = ',F9.5)
  16            FORMAT(1X,'k3 = ',F9.5)
  17            FORMAT(1X,'k2 = ', F9.5)
  20            FORMAT(1X,2(F12.9))
                STOP
                END
C
```

```
C
C
C
C
      SUBROUTINE RATE(TC,ACID)

C
C
C
      REAL K02,K(3),E2
      COMMON/KINCON/MF,K,PHI
C
C
C
C
      RT = (TC+273.16)*1.987
           K(2) = 2.832E9*ACID*EXP(-22070/RT)
           RETURN
           END
C
C
C
C
      SUBROUTINE RUNGE(DERIV,N,T,C,DC,DT)
C
C
      EXTERNAL DERIV
      DIMENSION C(N),DC(N),CC(10),CK(4,10),Z(4)
      DATA Z/0.0,0.5,0.5,1.0/
C
      CALL DERIV(T,C,DC,N)
      DO 100 I = 1,N
           CK(1,I) = DT*DC(I)
 100       CONTINUE
      DO 200 J = 2,4
           TT = T + Z(J)*DT
           DO 210 I = 1,N
              CC(I) = C(I) + Z(J)*CK(J-1,I)
 210          CONTINUE
           CALL DERIV(TT,CC,DC,N)
           DO 220 I = 1,N
              CK(J,I) = DT*DC(I)
              CK(1,I) = CK(1,I) + CK(J,I)/Z(J)
 220          CONTINUE
 200       CONTINUE
      DO 300 I = 1,N
           C(I) = C(I) + CK(1,I)/6
 300       CONTINUE
      T = T + DT
      RETURN
      END
C
```

```
C
C
C
C
C
C
      SUBROUTINE DERIV(T,C,DC,N)
C
C
      DIMENSION C(N),DC(N)
      REAL MF,K(3)
      COMMON/KINCON/MF,K,PHI
C
      DC(1) = -K(1)*C(1)
      DC(2) = (K(1)*C(1)-K(2)*C(2)-K(3)*C(1)*C(2))
      RETURN
      END

^Z
```