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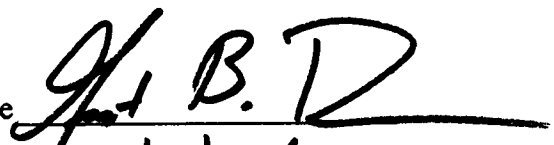
Signature 

Date 12/1/94

A MODEL OF A FIXED-FILM TRICKLE-FILTER BIOREACTOR FOR TRICHLOROETHYLENE DEGRADATION

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Grant Berkley Duncan

December 1994

DEDICATION

This thesis is dedicated to my Lord and Savior Jesus Christ, in whom all things are possible.

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The successful completion of a thesis is not accomplished without the assistance of many friends, family members, and faculty members. Special thanks go to the following:

I wish to thank the members of my committee, Dr. Weber and Dr. Donaldson, for their insight and helpful comments in shaping this thesis. The financial support provided by Dr. Donaldson is sincerely appreciated.

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ABSTRACT

A mechanistically-based model of a fixed-film trickle-filter bioreactor for co-metabolic degradation of TCE has been developed. This model incorporates diffusional and kinetic resistances and generates estimates of TCE stripped from the liquid by gas as well as the extent of biological degradation of TCE. The model predictions are consistent with a limited data base. It has isolated the kinetic resistance as the dominant resistance to the degradation of TCE. The model should be useful in determining the optimal conditions for minimizing the stripping of components of interest from the bioreactor liquid phase. It appears the model will be a useful design tool during scale-up operations.

PREFACE

A commentary on being an engineer:

It is a great profession. There is the fascination of watching a figment of the imagination emerge through the aid of science to a plan on paper. Then it moves to realization in stone or metal or energy. Then it brings jobs and homes to men. ...it elevates the standards of living and adds to the comfort of life. That is the engineer's high privilege.

The great liability of the engineer compared to men of other professions is that his works are out in the open where all can see them. His acts, step by step, are in hard substance. He cannot bury his mistakes in the grave like the doctors. He cannot argue them into thin air or blame the judge like the lawyers. He cannot, like the architects, cover his failures with trees and vines. He cannot, like the politicians, screen his shortcomings by blaming his opponents and hope the people will forget. The engineer cannot deny he did it. If his works do not work, he is damned.

Herbert Hoover

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NOMENCLATURE

a	gas-liquid interfacial area, area/volume
a'	liquid-biofilm interfacial area, area/volume
a_p	surface area of packing, area/volume
a_t	geometric area of the dry packing, area/volume
C_A	concentration of component A, mol/volume
C_{A0}	initial concentration of component A, mole/volume
C_L	liquid phase total molar concentration, mole/volume
D	diffusivity coefficient, area/time
d_p	diameter of the packing, length
G	total molar gas flow rate, mole/time
G'	gas flow rate, mole/area time
G''	gas flow rate, mole/time
k_i	reaction rate constant, 1/time
k	average reaction rate constant, 1/time
k_Ga	gas phase mass transfer coefficient, mole/volume time pressure

k_La	liquid-solid phase mass transfer coefficient, 1/time
k_S	liquid phase mass transfer coefficient at liquid-solid interface, length/time
K_Ga	overall gas-liquid mass transfer coefficient, mole/volume time pressure
K_Sa	overall liquid-solid mass transfer coefficient, 1/time
L	molar liquid flow rate, mole/time
L'	liquid flow rate, mole/area time
L''	liquid flow rate, mole/time
m	equilibrium constant, dimensionless
m*	coefficient in equation (1)
n	coefficient in equation (2)
n*	coefficient in equation (1)
N_Aa	gas-liquid molar flux of component A, mole/volume time
N'_Aa'	liquid-solid molar flux of component A mole/volume time
P_T	total pressure, pressure
Re	Reynolds Number
S	cross-sectional area
Sc	Schmidt Number

Sh	Sherwood Number
V	reactor volume
V_G	gas velocity, length/time
V_L	liquid velocity, length/time
x	mole fraction in liquid phase; x_i-mole fraction at gas-liquid interface; x_S- mole fraction at biomass surface; x_{in}-mole fraction entering increment; x_{out}-mole fraction exiting increment;
y	mole fraction in gas phase; y_i-mole fraction at gas-liquid interface; y_{in}-mole fraction entering increment; y_{out}-mole fraction exiting increment
z	column length, length
α_1	coefficient in equation 2
ϕ	fraction of packing that is wetted
β	coefficient in k_Ga correlation
ρ	density, mass/volume
ρ_p	density of packing, mass/volume
τ	residence time, time
μ	liquid viscosity, mass/ length time

INTRODUCTION

The use of trichloroethylene (TCE) in the United States began in the 1940's and was used extensively until the mid-1970's. Its many applications included dry cleaning, an extraction agent for the decaffination of coffee, and as a general anesthetic in dentistry and medicine [1]. However, its greatest use was as a degreasing agent. TCE's high solvency for oils, greases, waxes, lubricants, etc., combined with a non-corrosive and non-flammable nature, made it an attractive option in industrial degreasing applications. In 1974, approximately 90% of the TCE produced was used in this capacity, generating, according to the Environmental Protection Agency (EPA), approximately 310,000 tons of waste solvent [1].

In 1975, a study by the National Cancer Institute provided evidence that exposure to large concentrations of TCE caused tumors in mice [2]. The subsequent backlash led to a severe curtailment in its use, and the following year, it was added to the EPA's list of hazardous substances. However, much TCE already used and discarded was still present in the environment. For years, TCE had been considered non-toxic and its disposal after use was non-regulated. Decades of dumping waste solvent on the ground occurred before the discovery of its contamination of groundwater aquifers [1].

It soon was evident that the groundwater contaminated with TCE would require remediation. Because of its slight solubility in water and high volatility, air stripping followed by vapor recovery and carbon absorption became the most common treatments

[3]. However, these treatments can be quite costly. Additionally, these forms of treatment simply transfer the TCE to another medium, which also must be treated. Alternative methods for clean-up were sought that were not only cheaper, but also destroyed the contaminant.

In 1985 Wilson and Wilson described a novel approach to removing TCE from contaminated aquifers [4]. They hypothesized that a certain strain of bacteria which utilized methane as a carbon source would also degrade TCE. Their subsequent efforts to test this theory proved successful, as the bacteria removed 95% of the TCE that had been present in a spiked sample.

In 1988, Strandberg et al. constructed and operated 2 fixed-film trickle-filter bioreactors to evaluate the technical feasibility of employing methane-utilizing bacteria to treat TCE-contaminated groundwater [5]. After establishing a colony of bacteria proven to co-metabolize TCE in these bench scale reactors, these researchers passed a synthetic groundwater spiked with known levels of TCE through them. The effluent from several trials was then analyzed to determine the amount of TCE degraded by the bacteria.

The data from these experiments was utilized in the activity represented here. The goal of this research was to develop a mechanistically-based model describing the performance of the bench-scale reactors utilized by Strandberg et al. This computer model was then to be used to determine the rate-limiting step in the reaction, as well as provide a better understanding of the total mechanisms of TCE biodegradation. It was also expected that this work would provide an estimated of the rate constant for TCE

degradation. It was anticipated that the model developed in this activity would then be used at various stages in scale-up work to achieve the ultimate goal: the implementation of a full scale bioreactor operating in the field, remediating TCE-contaminated groundwater on a gallon per minute scale.

LITERATURE REVIEW

Contamination of groundwater by TCE has in recent years attracted national attention. Cleaning up these aquifers has become a priority. This literature review covers the major topics relating to the remediation of TCE-contaminated water by methanotrophic bacteria. The major topics of discussion are:

- Biological Degradation of TCE
- Modeling of Biological Degradation of TCE
- Mass Transfer Correlations
- Discussion of Mass Transfer Correlations

Biological Degradation of TCE

In 1985, J. T. Wilson and B. H. Wilson suggested a new way to treat TCE-contaminated groundwater [4]. They described the ability of the methane monooxygenase enzyme (MMO) produced by methanotrophs (bacteria which utilize methane as a food source) to oxidize and dechlorinate halogenated methanes. This knowledge, coupled with the capability of propane-oxidizing bacteria to epoxidate ethylene and then further metabolize the epoxide, led them to theorize that this enzyme was capable of reaction with TCE. They exposed soil to natural gas to enrich it for the growth of methanotrophs and for other bacteria capable of oxidizing alkanes present in the natural gas. The ability of the

soil to remove TCE from water was then determined by contacting the soil with contaminated groundwater. The results of their experiment showed a 95% removal of the TCE from the groundwater, as compared to "no statistically significant degradation" [4] in tests with the control sample (soil not pretreated with methane or exposed to methane during a 2 week trial). Additionally, their work was performed under aerobic conditions. This ability of this strain of bacteria to oxidize TCE is referred to as co-metabolism [6] (See Figure 1[1]. The bacteria do not utilize TCE as a food source; the enzyme simply is effective at oxidizing TCE). Subsequent efforts by Wilson et al. [6] and McClellen et al. [7] served to confirm the results of this initial work.

Little et al. [8] isolated a strain of bacteria from groundwater contaminated with TCE, and after a series of experiments proposed a mechanism for the biodegradation of TCE (see Figure 2). Their mechanism begins with the conversion of TCE to TCE epoxide, driven by the methane monooxygenase (MMO). This expoxide is then broken down in water to form dichloroacetic acid, glyoxylic acid, carbon monoxide, and formate. These compounds then further degraded to carbon dioxide.

Fliermans et al. [9] "investigated the activity and community structure" of bacteria taken from subsurface sediments which had been exposed to large concentrations of short-chained hydrocarbons, namely TCE. Like the results of the work by Little et al [8], they identified carbon dioxide as an end product; products of hydrochloric acid, lesser amounts of DCE, and possibly chloroform were also identified.

[1] All Figures located in Appendix A.

In 1988, Strandberg et al. constructed and operated 2 fixed-film trickle-filter bioreactors to evaluate the technical feasibility of employing methane-utilizing bacteria to treat TCE-contaminated groundwater [5]. The majority of the experimental runs were conducted with a bioreactor 5-cm in diameter, and 110-cm in length. This glass column was filled with 0.6-ceramic berl saddles to provide a support medium for the bacteria culture. (There were 2 bioreactors; 30-cm and 110-cm in length, identical otherwise. Initial tests were done with the 30-cm bioreactor, and subsequent work with the 110-cm bioreactor). They obtained a microbial consortium from TCE-contaminated groundwater on the Oak Ridge Reservation. The bacteria colony was established in the bioreactor by adding approximately 50 mL of actively growing culture and 150 mL of fresh mineral-salts medium and operating the system at near total recycle at 10 mL/min. A synthetic groundwater containing 1 mg/L TCE was fed at 0.1 mL/min. A co-current gas stream containing 20% methane and 80% air was introduced at 10 mL/min. After 3-4 weeks, a growth of salmon-pink biomass was visible throughout the column. This system was then switched to single-pass mode and the methane concentration reduced to typically 4% methane in air.

An aqueous feed solution containing mineral salts and TCE, DCE (dichloroethylene), or both was fed to the bioreactor where it was distributed over the top of the packing at 10 mL/min, typically. The influent concentrations of TCE and DCE were typically around 1 mg/L each. A co-current stream of 4% vol/vol methane and air was fed to the bioreactor at 20 mL/min. The bioreactor was operated at room

temperature (22-24 °C). TCE and DCE degradation was measured at liquid flow rates of 5, 10, 20, 35, and 50 mL/min. Strandberg et al. obtained a degradation rate of greater than 50% for TCE and greater than 90% for DCE with a residence time of around 50 minutes (single pass). The TCE degradation rate appeared to be first order in TCE concentration. Several other groups have also reported the TCE degradation rate to be first order in TCE concentration [3, 10-14].

Modeling of Bioreactors

In order to gain a better understanding of how biological systems utilizing methanotrophs to degrade TCE operate, models have been developed by various researchers. In order to accomplish this task, each researcher or group of researchers had to address how their model managed the kinetics of the biological reaction. Most chose either Monod type kinetics or a first-order approximation. Reviews of several studies of the biological degradation of TCE follow. These works are grouped according to their treatment of the kinetics.

Monod Kinetic Models

Strand et al. [15] developed a model describing the kinetics of methane-oxidizing bioreactors for the degradation of toxic organics using Monod type kinetics. Their model simulated the dual competition between methane and toxic organics for the enzymatic

oxidation by the MMO. The reasoning for using Monod type kinetics in the model was not given; the model integrated three second order equations located in another source (Baily and Ollis, 1977--reference in Strand et al.'s paper) that described the fate of methane, oxygen, and the toxic organic of interest. The model indicated that competition between methane and the toxics for oxidation by the MMO has a negative effect on the toxic organic degradation. The researchers suggested that a bioreactor utilizing the bacteria producing the MMO might have to be operated in a cyclical manner, with the degradation of the toxic organics taking place when the availability of methane is reduced. The work of Strand et al. [15] was not validated by any experimental data.. However, the competitive inhibition predicted by their work is validated by the work of others [16-18] which did include experimental verification.

Broholm et al. [16] developed a model which characterizes the degradation of TCE based on competitive inhibition (TCE versus methane). The model reasonably represented the laboratory data, and verified the existence of competitive inhibition. The decision to use Monod kinetics in this model was based on its use in other models describing mixtures of interacting substrates. Broholm et al. utilized the same source as Strand et al. [15] for their governing equation.

Anderson and McCarty [18] proposed a model for the co-metabolic degradation of TCE by methanotrophic bacteria incorporating Monod kinetics. The equations used were the same as those utilized by Strand et al. [15] and Broholm et al. [16]. The decision to use Monod kinetics was simply because that was generally the approach taken when

modeling bioreactors. According to Anderson and McCarty, their model does a reasonable job in predicting the TCE and methane fluxes, when compared to "observed and published values."

A First-Order Kinetic Model

Speitel and McCay's [17] activity focused on the removal of TCE from an air stream. Aside from the kinetic considerations, their work is interesting due to the use of methanotrophic bacteria in conjunction with other treatments such as air stripping and soil-vapor-extraction. This suggests the potential exists for using bioreactors to clean up air streams contaminated during groundwater remediation. They achieved removal efficiencies ranging from 20% to 80% with 5-12 minute gas phase residence times. Spietel and McCay's model actually is built assuming Monod kinetics. This, according to the researchers, was done to get the proper fit to the TCE degradation data. By assuming an arbitrarily large value for the half-saturation coefficient K_S, and adjusting the specific utilization rate k, they were able to generate a pseudo-first order rate constant, k_1 , from the ratio of k/K_S. Their model does a reasonable job of predicting TCE removal. The experimental bioreactor set-up was very similar to that built by Strandberg et al.

Other Modeling Efforts.

The modeling of bioreactors discussed so far centers around the destruction of TCE; additional models have been developed where TCE removal was not the focus. However, they warrant mention in this literature review because of their relevance to this work with regards to bioreactor modeling.

Monod Kinetics

San's [19] goal was to...

> ...obtain an analytical relationship between the biomass and the substrate concentrations and to express them as a function of hydraulic residence time and other parameters using Monod kinetics in differential mass balance equations at steady-state conditions.

He developed simultaneous differential equations, assuming plug flow, by performing mass balances around an infinitesimal volume element; these equations were then solved analytically. He showed that the analytical solution was more easily obtained than by the finite difference solution method for the original differential equations. San used Monod kinetics because of their extensive use in describing bioreactors for an extended period of time, and because the validity of the Monod kinetic model has " been verified both theoretically and practically."

Suidan et al.'s [20] efforts resulted in the generation of nomograms which provide quick estimates of biofilm performance as a function of process parameters governing the operation of biofilm reactors. By using simple algebraic equations relating the flux of the substrate of interest to the bulk phase substrate concentration, the boundary layer thickness, and the minimum substrate concentration necessary to sustain biological growth (all in dimensionless form), the authors present a graphical procedure for designing completely-mixed and plug-flow bioreactors. They are careful to point out that the nomograms do not take into account substrate competition, and the reaction of the substrate of interest is assumed to be the rate-limiting step. Their use of Monod kinetics was based on the fact that they had generally been used in the effort to model the kinetics of other bioreactors.

First Order Kinetics

Hamoda's work [21] involved obtaining data from a four-stage aerated submerged fixed-film reactor treating synthetic carbonaceous wastewater; the bioreactor performance was modeled based on Monod kinetics. Although the bioreactor used by Hamoda differs from the one Strandberg et al. [5] built and operated (and from other bioreactors considered in this review), his conclusions regarding the bioreactor's first order kinetic approach bears mentioning:

A steady-state mathematical model with substrate-limiting phenomena based on Monod growth kinetics can successfully describe reactor performance and biomass growth. This appears to be valid, however, for the first stage of the reactor. The substrate removal in the last stages of the reactor, receiving a low substrate concentration, can be better described by first-order kinetics.

Golla and Overcamp [22] developed " simple, analytical models...to approximate the steady-state concentration and biofilm thickness in a biofilm reactor." The models assumed plug flow in one case, and longitudinal dispersion of substrate in the other. These models were developed with first order kinetics from the start. The authors warn that this assumption precludes the use of the model for higher substrate concentrations, in agreement with Hamoda [21].

Their longitudinal dispersion model agreed with results they used for comparison; the plug flow model however, over-predicted substrate concentration at the reactor inlet and utilization and under-predicted it downstream. They attributed this to the neglect of dispersion effects.

Mass Transfer Correlations for Trickle Beds

A review of the literature regarding mass transfer in trickle filter reactors yielded 3 mass transfer correlations; $k_G a$ for the gas phase, $k_L a$ for the liquid phase, and k_S for the liquid region adjacent to the solid phase, which in this case, represents transfer across the

liquid-biofilm interface. The following discussion will focus on relevant information related to these correlations. Discussion of their suitability will follow.

Gas-Phase Mass Transfer

Shende and Sharma [23] conducted a series of experiments with 10-, 15-, and 20-cm i.d. packed columns operating in co-current downward operation with a variety of packing material in order to determine the effective interfacial area. Superficial gas velocities ranged from 50-300 cm/sec; superficial liquid velocities from 0.1-3.5 cm/sec. In addition, values of gas side mass transfer coefficients were obtained by absorbing lean sulfur dioxide into an aqueous caustic soda solution. Packings studied included 1-inch ceramic Intalox saddles (using the 20-cm i.d. column), 1-inch polypropylene Pall rings (using the 20-cm i.d. column), and 5/8-inch stainless Pall rings (using the 10-cm i.d. column) as column packing material. The results of their experiments included a multiple regression correlation for the gas side mass transfer coefficient, k_Ga, units of $\frac{gmol}{cm^3\ sec\ atm}$:

$$k_Ga = \beta V_G^{m^*} V_L^{n^*}. \qquad (1)$$

V_G and V_L are the superficial gas and liquid velocities, respectively, in cm/sec. The values for β, m^*, and n^* depend on the size and type of packing used; for the model developed in this activity, the values for the 5/8-inch stainless Pall rings were used, as this was the

closest in size to the type used in the experiments by Strandberg et al. [5]. Those experiments were conducted using 0.6-cm berl saddles. The prediction of the correlation when for 5/8-inch pall rings was very close to the experimental data when superficial gas velocities of 0.5, 1.0, and 1.5 cm/sec were used. For comparison, the typical value for the superficial gas velocity in Strandberg et al.'s work was around 0.02 cm/sec.

Liquid Phase Mass Transfer at Gas-Liquid Interface

Mahajani and Sharma [24] determined values of the effective interfacial area and liquid side mass transfer correlations in trickle bed reactors. Their experiments were conducted using a 4.6-cm i.d. glass column, with a packed height of around 10 cm. The packing material was activated carbon pellets (2.5 mm x approximately 4 mm) and carbon granules (approximately 5 mesh). Their column was operated in co-current downward fashion. In order to measure the value of k_La, pure CO_2 was absorbed into aqueous solutions of sodium hydroxide. Mahajani and Sharma [24] fit their experimental values of k_La, units of sec^{-1}, with the following correlation:

$$k_La/D = \alpha_1[G'/\mu]^n[\mu/\rho D]^{.5} \qquad (2)$$

G′ is the liquid mass velocity in g/cm^2 s; D is the diffusion coefficient in cm^2/sec; α_1 and n were determined by Mahajani and Sharma [24]. The liquid superficial velocities used in

Mahajani and Sharma's work ranged from approximately 0.1 to 0.3 cm/sec. For the sake of comparison, Strandberg et al. [5] operated their column at a typical superficial liquid velocity of 0.008 cm/sec. The correlation proposed by Mahajani and Sharma fit their experimental results very well.

Liquid Phase Mass Transfer at Liquid-Solid Interface

Satterfield et al. [25] determined the liquid-solid mass transfer coefficient in packed beds with co-current downward flow. They measured the rate of solution of cylindrical 3- or 6-mm benzoic acid tablets in water in the presence of nitrogen, helium and argon. The experimental apparatus used for these determinations was a glass column with an i.d. of 7 cm, an a length of approximately 70 cm. The correlation developed to model the experimental results, units of m/s, is as follows:

$$\frac{Sh\phi}{Sc^{1/3}} = 0.266Re^{1.15} \qquad (3)$$

Where Sh is defined as $k_S d_p/D$, and ϕ is the fraction of the surface of the packing that is wetted. Gas flow rates were varied between 0-1.6 kg/m^2 s; the typical value for the gas rate in Strandberg et al.'s study was 0.019 kg/m^2 s. Liquid flow rates for Satterfield et al.'s experiment ranged form 0.5 to 25 kg/m^2 s; the typical value in Strandberg et al.'s [5]

work was approximately 0.1 kg/m² s. ϕ is generated from a correlation taken from a paper published by Mohunta et al. [26]:

$$\phi = 1 - 1.02^{e^{-0.278(L/a_t \mu)^{0.7}}} . \qquad (4)$$

Effective Interfacial Area, Liquid-Solid Boundary

As an approximation, the effective interfacial area was assumed to be equal to the product of the density of the packing (.6-cm Berl saddles) and the interfacial area/mass of the packing. This approach is making the assumption that the effective biomass " area" available for contact with the TCE is the fraction of the packing that is wetted (as estimated by the correlation of Mohunta et al. [26].

$$a' = \rho_p a_p \phi. \qquad (5)$$

Discussion on Mass Transfer Correlations

The goal of the work undertaken in this study was to develop a model for TCE degradation by methanotrophic bacteria in packed towers based on fundamental physical and chemical engineering principles. This work utilizes data from the bench-scale bioreactor built and operated by Strandberg et al. to substantiate this model. The model

developed in this activity evolved via comparison of the model predictions with the experimental results of Strandberg et al. [5] and Garland et al. [28]. A model of this type, incorporating mole balances with other correlations representing transport and reaction rates, allows predictions of the capability of a proposed design to accomplish the objectives intended. In this case, the ultimate goal is the development of a large-scale bioreactor capable of degrading TCE.

The mechanistic approach taken in this model development allows one to estimate the contribution of the various mass-transfer resistances to the model's overall predictive capabilities. The development of the mole-balance equations and the method chosen for their solution are based on a typical chemical engineering approach to mass-transfer/kinetic problems. The reliability and performance of this approach have been verified by years of use in many different applications. The model does however, involve extrapolation of predictive equations for mass transfer components. If there is a weakness in the model's development, it is in the use of the mass transfer correlations discussed in this review.

The largest application of trickle filter reactors is in the chemical industry. In general, the conditions under which these reactors operate is vastly different from the bioreactor of interest here, in terms of temperature, pressure, and flows. No consideration was given to biological activity or applications by these researchers. Although every effort was made to find correlations whose developmental conditions matched those of the bioreactor, the fact remains that for the most part, the conditions under which the mass-

transfer correlations were developed was different that those of the current application were different when a comparison is made.

MODEL DEVELOPMENT

The development of the steady-state model describing bio-oxidation of TCE in the bioreactor is based on a steady-state molar balance around an incremental volume of the reactor. Molar balances are determined for the flow of liquid and gas through the incremental volume.

Incremental Gas Volume

For the gas flow:

moles of component A entering increment	=	moles of component A exiting increment	+	moles of component A absorbing into liquid phase

Stated mathematically:

$$Gy_{in} = Gy_{out} + N_A a \Delta V \qquad (6)$$

Rearranging and dividing by -1 yields:

$$Gy_{out} - Gy_{in} = - N_A a \Delta V \ . \qquad (7)$$

The quantity Δy represents $y_{out} - y_{in}$; ΔV is defined as $S\Delta z$. Substituting these definitions into (7) yields:

$$G\Delta y = -N_A a S \Delta z \quad . \qquad (8)$$

Dividing by $S\Delta z$ and letting G' equal to G/S, equation (8) becomes:

$$G' \frac{\Delta y}{\Delta z} = - N_A a \quad . \qquad (9)$$

Taking the limit as Δz approaches 0 and dividing by G' yields:

$$\frac{dy}{dz} = - \frac{N_A a}{G'} \quad . \qquad (10)$$

Equation (10) is the governing equation for mass transfer to and from the gas phase. Utilizing the film theory for mass transfer, the gas phase flux of the absorbing component may be reasonably represented by:

$$N_A a = k_G a P_T (y - y_i) \quad . \qquad (11)$$

The flux through the liquid film adjacent to the gas-liquid interface may also be reasonably represented by:

$$N_A a = k_L a C_L (x_i - x) \quad . \tag{12}$$

By definition,

$$\frac{1}{K_G a P_T} = \frac{1}{k_G a P_T} + \frac{m}{k_L a C_L} \quad , \tag{13}$$

where m is equal to y/x. From which follows:

$$N_A a = K_G a P_T (y - mx) \quad . \tag{14}$$

Equation (14) defines the overall flux across the gas-liquid interface. Substitution of equation (14) into equation (10) yields:

$$\frac{dy}{dz} = - \frac{K_G a P_T}{G'} (y - mx) \quad . \tag{15}$$

Incremental Liquid Volume

The molar balance equation for flow of liquid through the incremental volume is developed similarly to that for the gas phase:

moles of component A entering increment	+	moles of component A absorbing from gas phase	=	moles of component A exiting increment	+	moles of component A absorbing into biomass

In an expression similar to (6), the above balance can be represented by:

$$Lx_{in} + N_A a\Delta V = Lx_{out} + N'_A a'\Delta V. \qquad (16)$$

Rearranging and dividing by -1 yields:

$$Lx_{out} - Lx_{in} = N_A a\Delta V - N'_A a'\Delta V. \qquad (17)$$

The quantity $x_{out} - x_{in}$ can be represented by Δx; and ΔV is $S\Delta z$. Using these definitions, equation (17) becomes:

$$L\Delta x = S\Delta z(N_A a - N'_A a'). \qquad (18)$$

Dividing by $S\Delta z$ and replacing L/S with L′ yields the following:

$$L' \frac{\Delta x}{\Delta z} = N_A a - N'_A a' \quad . \qquad (19)$$

By taking the limit as Δz approaches 0 and dividing by L′, equation (20) is obtained; this provides the overall governing equation for the liquid phase molar balance for component A:

$$\frac{dx}{dz} = \frac{N_A a}{L'} - \frac{N'_A a'}{L'} \quad ; \qquad (20)$$

where N'_A is the flux of component A at the surface of the biofilm and a' is the interfacial area of biofilm per volume of bioreactor.

Again, utilizing the film theory for mass transfer, the flux through the liquid film region adjacent to the biofilm surface is reasonably represented by:

$$N'_A a' = k_S a' C_L (x - x_S) \quad . \qquad (21)$$

The reaction rate is postulated to be first order in TCE concentration (as reported in [3, 5, 10-14]). It may be defined in terms of biomass surface area and related to the flux as:

$$N'_A a' = k_i C_L x_S \quad . \qquad (22)$$

Utilizing the definition

$$\frac{1}{K_S a C_L} = \frac{1}{k_S a' C_S} + \frac{1}{k_i C_L} \quad , \qquad (23)$$

equations (21) and (22) may be reasonably represented as:

$$N'_A a' = K_S a C_L x \quad . \qquad (24)$$

The selection of the mass transfer correlations and a discussion of their appropriateness for the model can be found in the literature review.

The values of m, Henry's constant, for TCE was found in the work of Miller et al. [27]. Experimental performance data and operating conditions from Strandberg et al. [5] were used to define the conditions needed to estimate $k_G a$, $k_L a$, k_S.

The model tracks the movement of 6 components in the gas and liquid phases down the length of the bioreactor in adjustable incremental column lengths (typically in 10-cm increments for the results described by this thesis). The components included in the model, in addition to TCE, are hydrochloric acid (HCl), methane (CH_4), oxygen (O_2), carbon dioxide (CO_2), and dichloroethylene (DCE). Equation (15) describes the

movement of the components between the gas and liquid phases; Equation (24) governs the flux across the liquid-solid interface. Each component is represented by an equation (15) and (24) in the computer simulation.

The set of first order differential equations represented by Equations (15) and (24) is an initial-boundary-type of problem and was solved by 7th order Runge-Kutta integration with step-size control [29].

A value of the reaction rate constant k_i was calculated for each experimental data point as that necessary for the model-predicted bioreactor performance to match that of the experiment. It must be noted that the kinetic constants reported in this work are for TCE disappearance only. The experimental data collected concerned only TCE and DCE. Future work may include some analyses for the other components mentioned here, which will allow the model to predict the disappearance or appearance of the particular compound of interest. The model is capable of modeling of the disappearance of DCE should it become desirable to do so.

RESULTS & DISCUSSION

Determination of Kinetic Constant for TCE Degradation

As mentioned in the model development section, a reaction rate constant, k_i was determined for each experimental run by an iterative method. In this procedure, a reaction rate constant was first assumed and the model used this value to predict the amount of TCE that disappeared from the liquid phase. Once the model-generated disappearance agreed with the experimental value, it was assumed that the correct reaction rate constant for that particular run had been determined. The regressed kinetic constants and other experimental information are found in Table 1[2].

Examination of Table 1 reveals a very limited data base. Although the twenty-four data points exhibit much scatter, it was the opinion of the original researchers and this author that none of the data points would be discarded, even though it may have been possible statistically. It should also be noted that the first six runs in Table 1 were conducted using the 30 cm bioreactor.

It must be remembered that the facilitators of chemical reaction in this work are living organisms, which may be affected by many environmental conditions. These effects can reasonably be expected to impact the performance of the bioreactor in a positive, or conversely, negative manner, and may account for the wide range of regressed reaction

[2] All Tables located in Appendix B.

rate constants. The determination of the source of the scatter is beyond the scope of this effort. Therefore, it was decided to use the results of all the runs associated with the bioreactor, and an average resulting value of 6.7×10^{-3} min^{-1} for the reaction rate constant k_i was used in subsequent analyses of the model's validity and predictions.

Model Performance

Time Adjusted Kinetic Constant

The results of the determination of the individual kinetic rate constant, k_i, for each run are presented along with the experimental conditions from Strandberg et al. [5] and Garland et al. [28] in Table 1. As noted previously, the average of the regressed kinetic constants is 6.7×10^{-3} min^{-1}. To compare the kinetic rate constant of this activity to those published by Strandberg et al. [5], the time basis must be adjusted.

Equation (25) is the rate equation for a first order reaction [30]:

$$\ln\frac{C_{A0}}{C_A} = k\tau. \qquad (25)$$

Since both of these sources utilize a first order reaction rate for the disappearance of TCE, the product $k\tau$ must be equal for both sources of the reaction rate constants:

$$k_1\tau_1 = k_2\tau_2. \qquad (26)$$

Rearranging yields:

$$k_1 = k_2\frac{\tau_2}{\tau_1}. \qquad (27)$$

For a liquid rate of 20 cm^3/min and other experimental conditions as Run 20 of Table 1, the superficial liquid residence time for the present model is 108 min. The mean liquid residence time from Strandberg et al. [5] is 30 min. By multiplying the kinetic constant from the model, 6.7 x 10^{-3} min^{-1} by the ratio of 108/30, a value of 2.4 x 10^{-2} min^{-1} is obtained. This falls within the range of 1.0 x 10^{-2} to 4.6 x 10^{-2} min^{-1} obtained by Strandberg et al. [5].

Test for Parameter Effects

In addition to the model verification method discussed above, another check of the model's utility is whether its predictions are reasonable when the liquid and gas rates in the experimental bioreactor were varied. The model predictions for TCE removed by stripping are compared with experimental data in Figures 3 and 4. The kinetic constants are then compared versus the time since the experimental series of runs was begun and with the experimental gas and liquid rates and methane concentration (Figures 5, 6, and 7). The kinetic constants are not expected to exhibit any dependence on the liquid or gas rates and any such variation would be interpreted as an indication of a poor model.

The model was calibrated using data for the removal of TCE from the liquid phase as indicated by liquid influent and effluent compositional analysis. The removal of TCE from the liquid phase involved two simultaneously-occurring phenomena. TCE was removed from the liquid phase by destruction--that is, oxidation by the biofilm--and by stripping, which was the transfer of TCE from the liquid phase to the gas phase. For analyzing these effects, the individual kinetic constants for each run were used.

Liquid Rate Variation

Five runs (19, 21-24) conducted at discrete liquid rates were chosen in order to determine the amount of TCE stripped from the liquid phase by the experimental bioreactor. The gas rate and methane concentration in the gas phase were the same for all 5 runs. Figure 3 provides a comparison of the model predictions versus experimental data. It appears that the model does a reasonable job of predicting the bioreactor's behavior. In almost every case, it does over-predict TCE stripping; however, this difference shrinks with increasing liquid rate.

Gas Rate Variation

Efforts were made to choose a range of gas rates that varied in which the other parameters were held constant. Due to the repetitive nature of the experimental data with regard to gas rate, only 3 runs with the 30-cm reactor could be found where the bioreactor was operated over a range of gas rates. The methane concentration in the gas phase did

vary; however, the liquid rates were constant. Figure 4 presents a comparison of the effect of variable gas rates on stripping effects. It appears once again, that the model over-predicts the stripping observed in the bioreactor tests.

Analysis of Kinetic Constants

Figure 5 is a plot of the reaction rate constant versus the time since the beginning of the series of experiments. It reveals a large amount of data scatter among two discernible groups of data (i.e., less than or equal to 20 days after initiation of tests, and greater than 60 days after initiation of tests). The experiments reported in Table 1 were conducted over a period of time from late April to mid-August 1988. The individual kinetic constants regressed are displayed in Figure 3. As stated previously, the model was used to simulate the performance of two separate bioreactors, one 30-cm long and the other 110-cm long (both were the same diameter). The first six experiments, conducted in April and May, utilized the original 30-cm packed bioreactor. The packing material and biofilms were then transferred to a 110-cm column of the same diameter, new packing was added to fill the bottom of the column, and the established "seed" biofilms and packing were placed on the top of the new column. After an acclimation period in May and June, data were then collected again, as represented by the rate constants on the right side of Figure 5 (points older than 60 days).

Both groups of data obviously have considerable scatter; nevertheless, the first group early in the test program tends to have generally larger values of k_i than the second group later in the test program. This result is consistent with the two different bioreactors described above. The 30-cm bioreactor was observed by the original researchers to have a higher biofilm loading per unit volume of bioreactor (or per unit surface area of packing) than did the 110-cm bioreactor. This condition would tend to yield smaller rate constants for the 110-cm bioreactor than for the 30-cm bioreactor under the model conditions for which the specific bioreactivity was assumed to be constant and uniform. In general, the kinetic constants are quite similar in magnitude for both groups of data.

Effect of Independent Variables

The original researchers were interested in quantifying any effects of the independent variables (gas and liquid rates, methane concentration). Variation in the gas and liquid rates appear to be reasonably well accounted for in the model produced in this activity.

Liquid Rate

Figure 6 is a plot of the regressed reaction rate constant vs. the liquid rate. No trend is observable. This supports the premise that the model reasonably accounts for variation in the liquid rate.

Gas Rate

Figure 7 is a plot of the regressed reaction rate constant versus the gas rate. Although a trend may be discernible, maintaining the simplicity of the model at this early stage of development warrants disregarding any possibility of a trend in this analysis.

Methane Concentration

Figure 8 was generated to determine the effect of methane concentration on the reaction rate constant. No trend is observable from this comparison. Without further data, there is no reason to complicate the model by including effects of methane on the kinetics.

The planned operation of a field scale bioreactor should yield more data taken over a wider range of operating conditions. This should afford the researcher the opportunity to further substantiate the reliability of the model produced in the current activity.

Mass Transfer Resistances vs. Kinetic Resistance

Of particular interest is the role of mass transfer relative to reaction rate in the performance of the bioreactor. It would be very useful to determine whether the rate limiting step was due to mass transfer resistances or kinetic resistance. Table 2 summarizes the model's predictions using the individual regressed kinetic constants.

Overall, the kinetic resistance is the dominant effect, followed by the gas-phase resistance. Little liquid-phase diffusional resistance at the gas-liquid interface or resistance at the liquid-biomass interface is indicated.

CONCLUSIONS AND RECOMMENDATIONS

The mechanistic mathematical model reasonably predicts the performance of the bench-scale results and trends in the data. It has isolated the kinetic resistance as the dominant resistance to the degradation of TCE. It appears to be potentially useful in determining the optimal conditions for minimizing the stripping of components of interest from the reactor. It should prove to be a valuable tool for scale-up operations regarding the development of large-scale bioreactors for the oxidation of TCE. Further development of the model using the results from larger-scale bioreactors will be helpful in establishing this approach as a useful design tool.

The model is developed on sound fundamental concepts of mass transfer and chemical reaction. The mass-transfer correlations used are thought to be the best available. There is, however, considerable extrapolation and assumptions in their use in this work. Further model improvement may be possible if the fraction coverage of the packing could be better estimated and selected mass transfer coefficients are evaluated at conditions more relevant to this and future studies of TCE degradation by methanotrophic bacteria in packed towers.

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APPENDICES

APPENDIX A: FIGURES

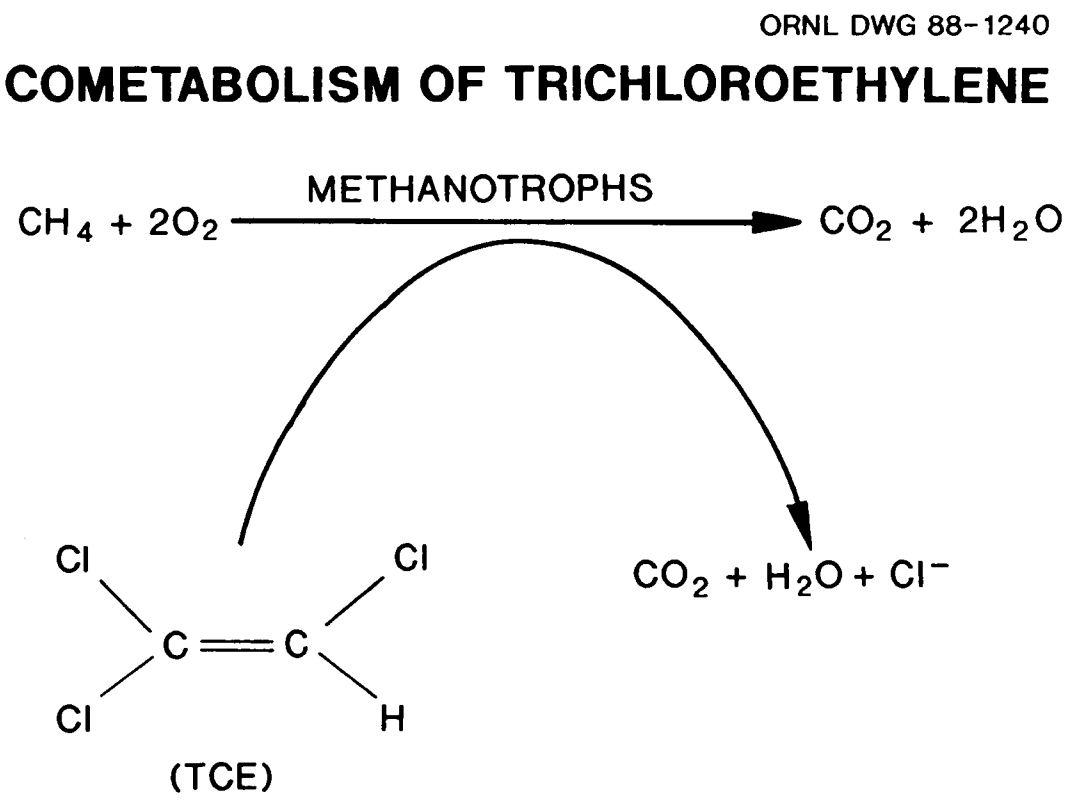

Figure 1: Co-Metabolism of Trichloroethylene

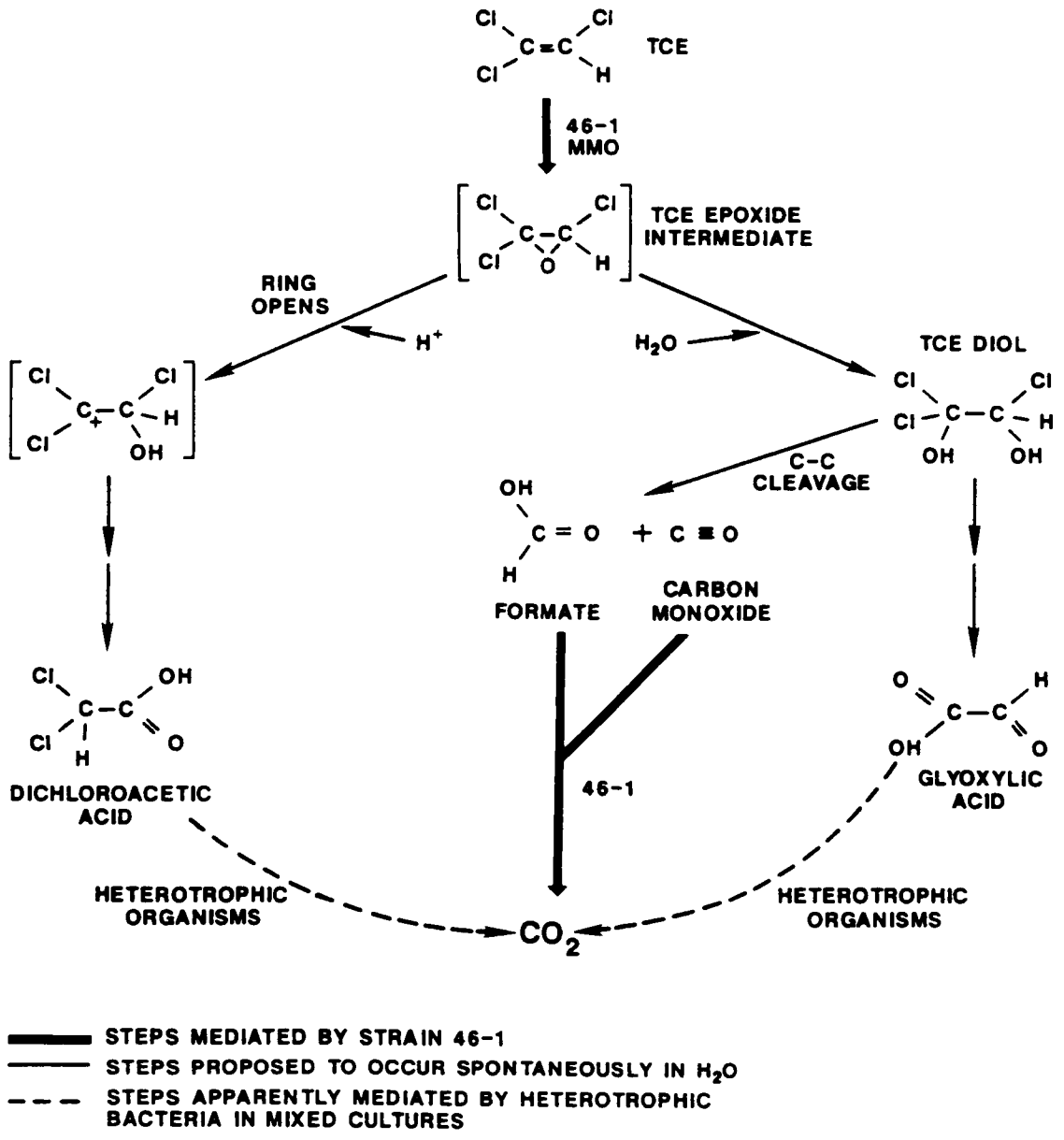

Figure 2: **Mechanism for TCE Degradation as Proposed by Little et al. [8]**

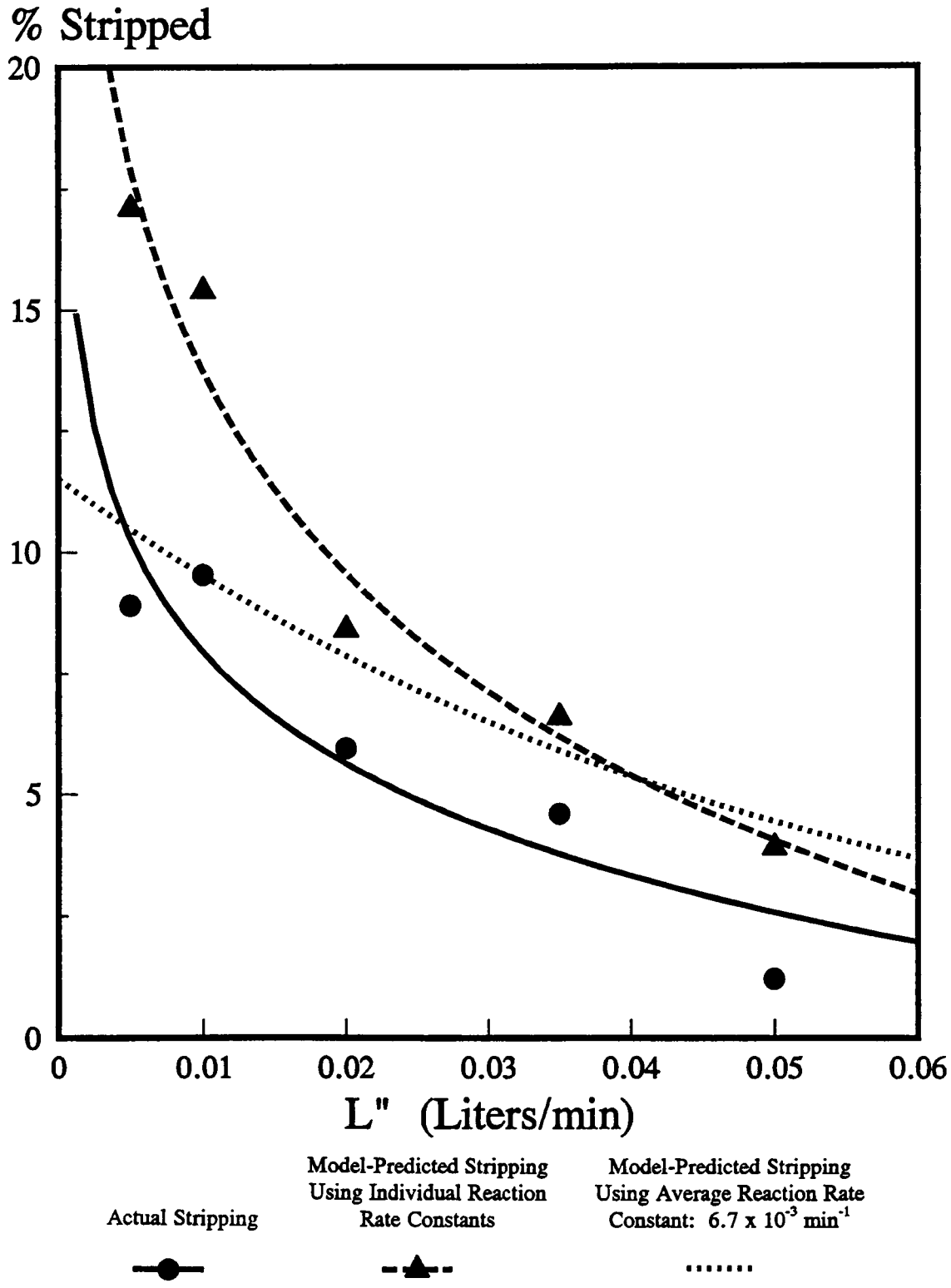

Figure 3: **Actual versus Model-Predicted Stripping Effects versus Liquid Rate. Other Variables Held Constant.**

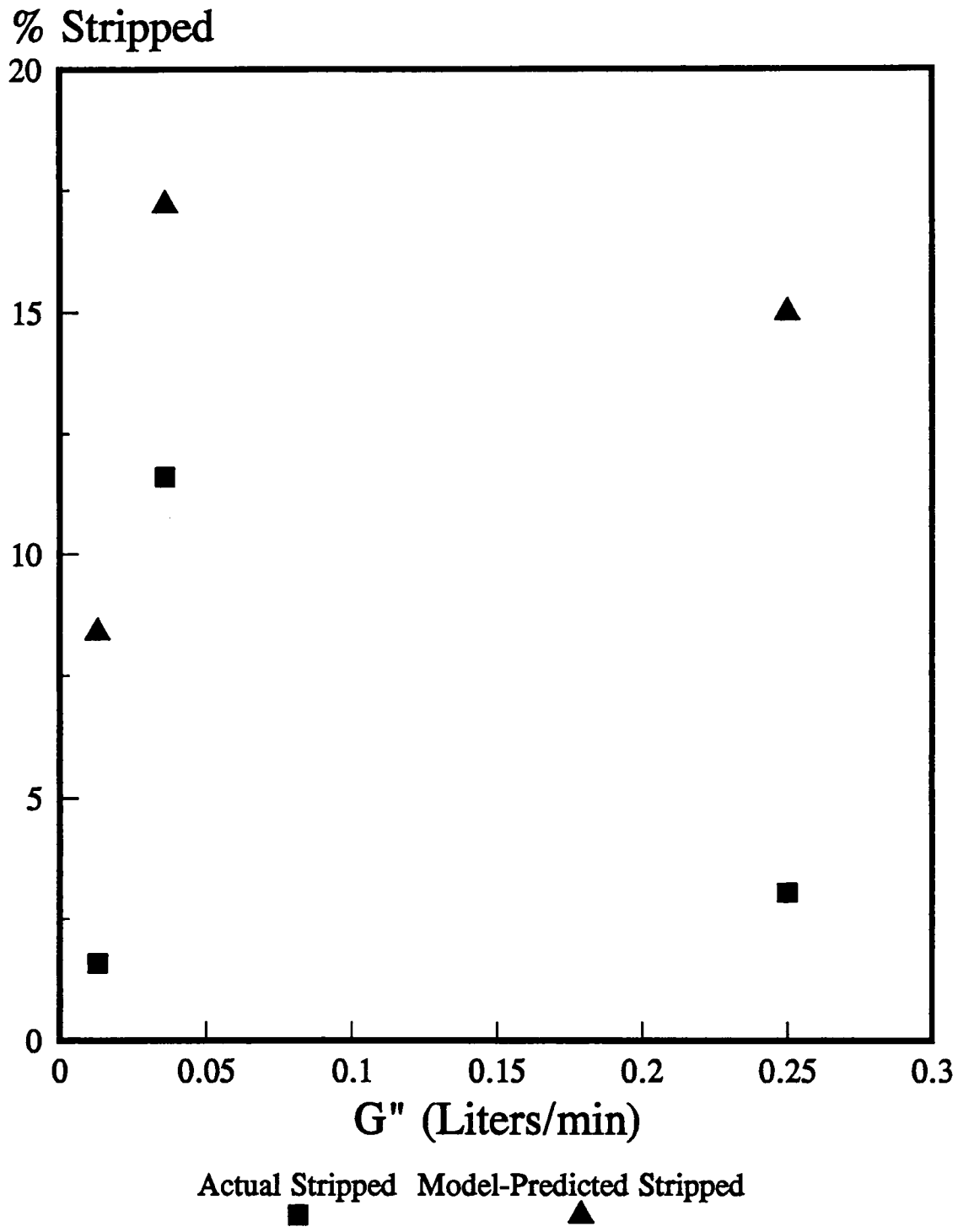

Figure 4: **Actual versus Model-Predicted Stripping Effects versus Gas Rate. Other Variables Held Constant. Individual Rate Constants for each Run used in the Model Predictions.**

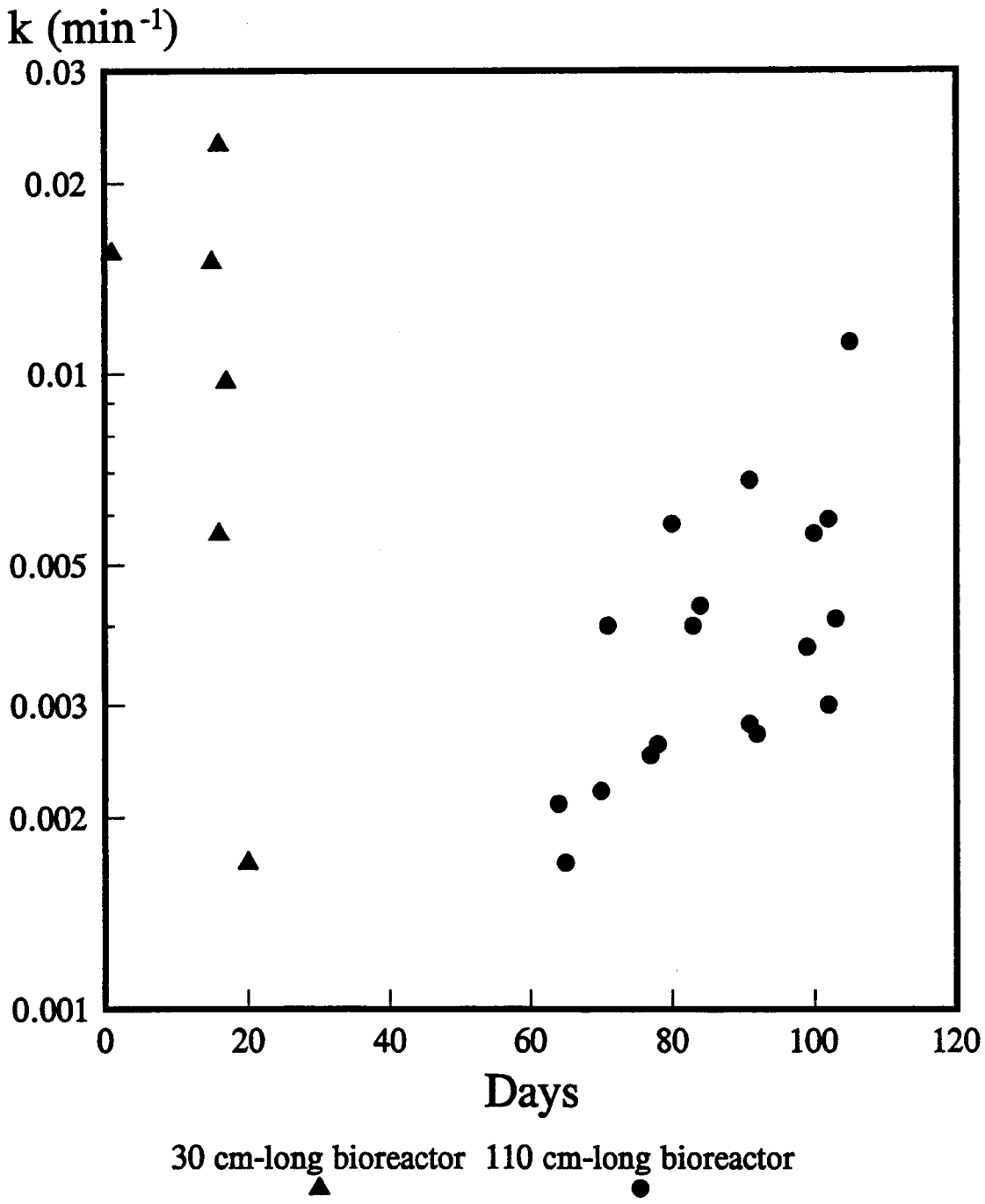

Figure 5: Reaction Rate Constant versus Experimental Duration

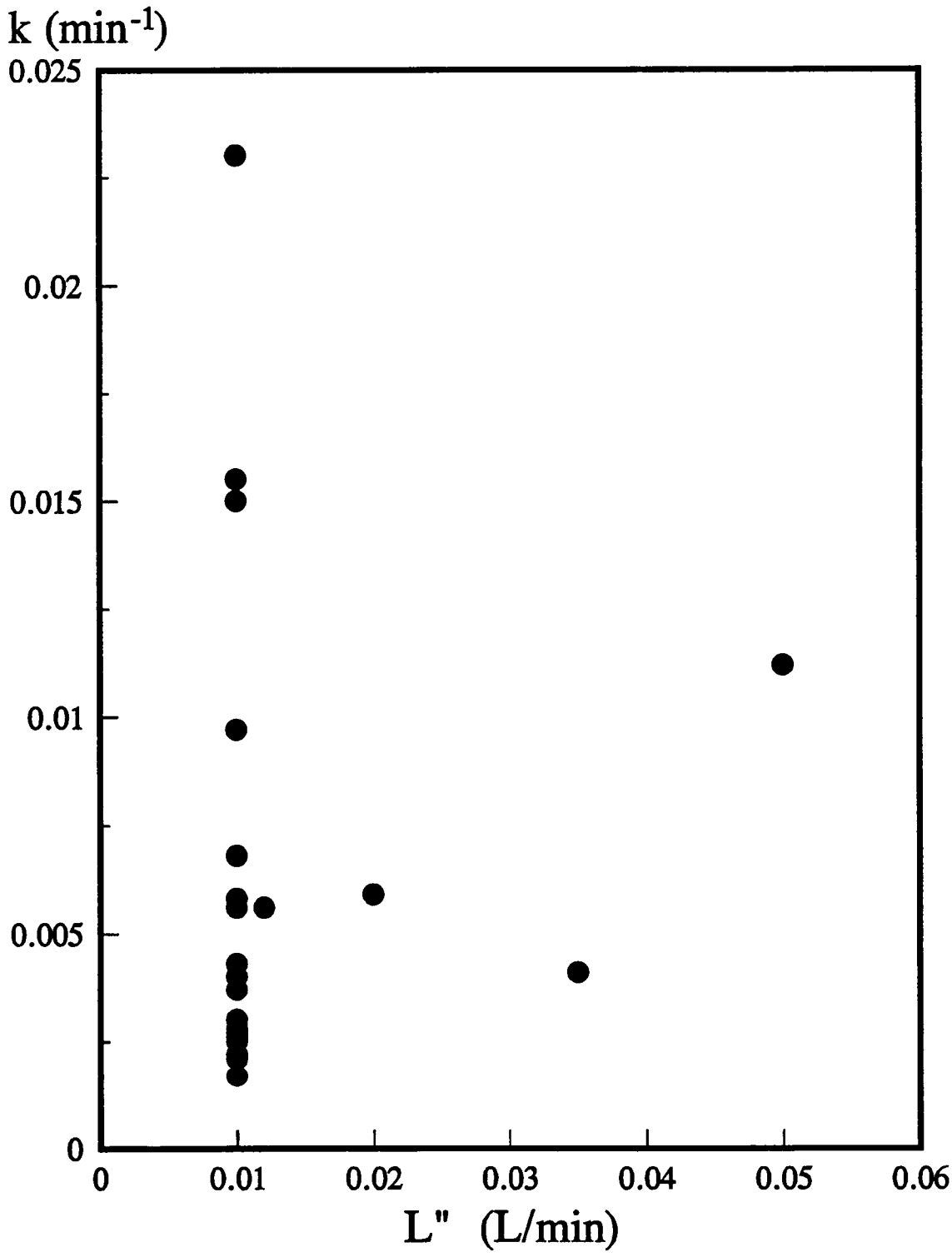

Figure 6: Reaction Rate Constants versus Liquid Rate

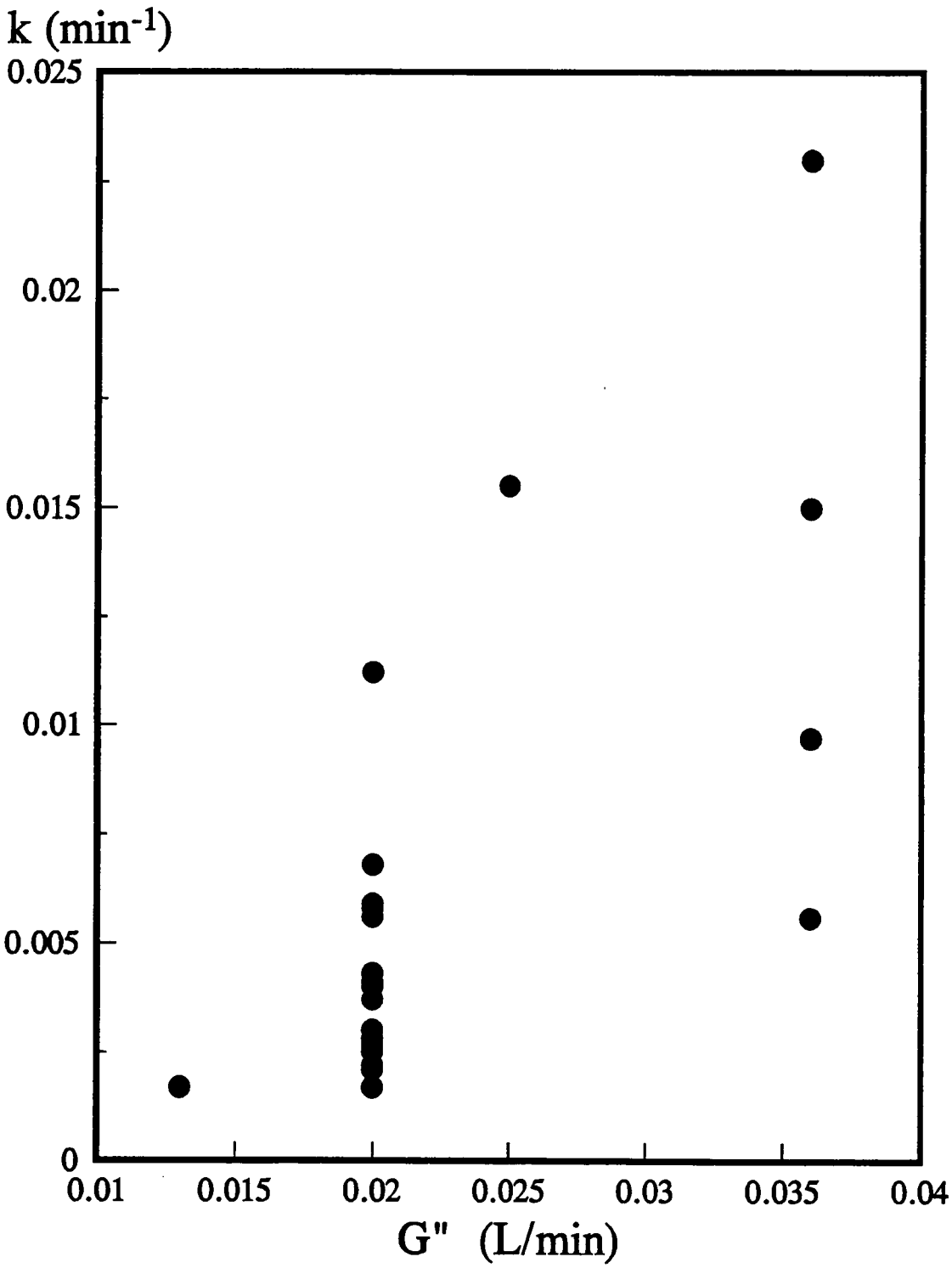

Figure 7: Reaction Rate Constants versus Gas Rate

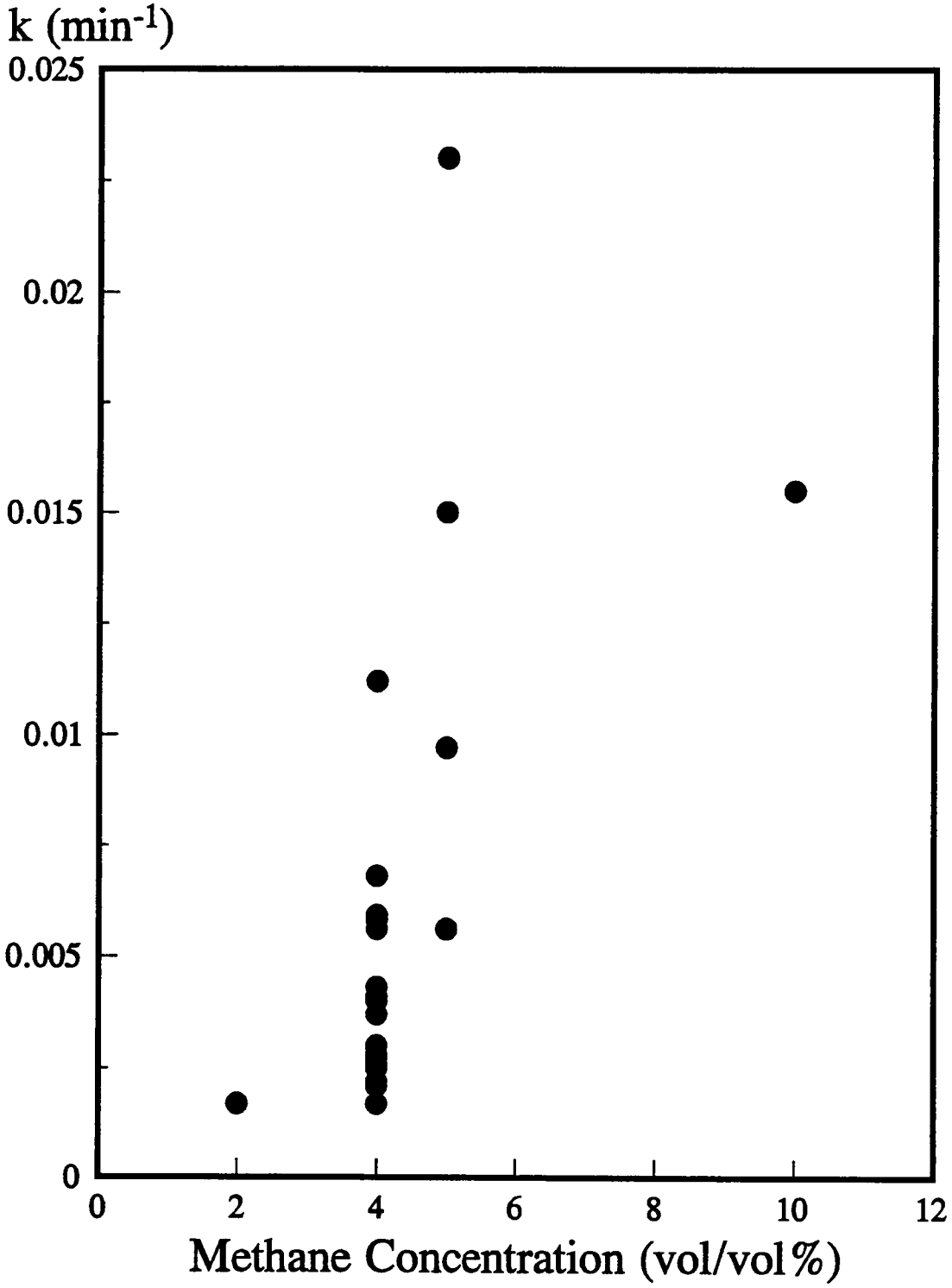

Figure 8: Reaction Rate Constants versus Methane Concentration

APPENDIX B: TABLES

Table 1: **Individual Kinetic Rate Constants and Original Data Base from Strandberg et al. [5] and Garland et al. [28].**

Run	Liquid Rate (L/min)	Gas Rate (L/min)	Influent Methane Concentration (%)	Influent Liquid Phase TCE (mole fraction)	Reaction Rate Constant (min-1)
1	0.01	0.025	5	5.62×10^{-8}	15.5×10^{-3}
2	0.01	0.036	5	6.71×10^{-7}	15.0×10^{-3}
3	0.01	0.036	5	4.25×10^{-8}	23.0×10^{-3}
4	0.012	0.036	5	7.13×10^{-7}	56.0×10^{-4}
5	0.01	0.036	5	1.12×10^{-7}	97.0×10^{-4}
6	0.01	0.013	2	1.12×10^{-7}	17.0×10^{-3}
7	0.01	0.02	4	1.06×10^{-7}	21.0×10^{-4}
8	0.01	0.02	4	7.26×10^{-8}	17.0×10^{-4}
9	0.01	0.02	4	8.91×10^{-8}	22.0×10^{-4}
10	0.01	0.02	4	6.71×10^{-8}	40.0×10^{-4}
11	0.01	0.02	4	9.04×10^{-8}	25.0×10^{-4}
12	0.01	0.02	4	8.36×10^{-8}	26.0×10^{-4}
13	0.01	0.02	4	1.19×10^{-7}	58.0×10^{-4}
14	0.01	0.02	4	6.03×10^{-8}	40.0×10^{-4}
15	0.01	0.02	4	8.08×10^{-8}	43.0×10^{-4}
16	0.01	0.02	4	9.87×10^{-8}	68.0×10^{-4}
17	0.01	0.02	4	1.11×10^{-7}	28.0×10^{-4}
18	0.01	0.02	4	1.14×10^{-7}	27.0×10^{-4}
19	0.005	0.02	4	1.23×10^{-7}	37.0×10^{-4}
20	0.01	0.02	4	1.37×10^{-7}	56.0×10^{-4}
21	0.01	0.02	4	1.51×10^{-7}	30.0×10^{-4}
22	0.02	0.02	4	1.37×10^{-7}	59.0×10^{-4}
23	0.035	0.02	4	1.51×10^{-7}	41.0×10^{-4}
24	0.05	0.02	4	1.37×10^{-7}	11.2×10^{-3}

Table 2: Model-Predicted Mass Transfer and Kinetic Constant Resistances.

Run	k (min^{-1})	$\frac{1}{k_G a}$	$\frac{1}{k_L a}$	$\frac{1}{k_S a'}$	$\frac{1}{k_i}$
1	15.5×10^{-3}	58.18	3.78	5.52	32.52
2	15.0×10^{-3}	49.72	4.43	6.47	39.38
3	23.0×10^{-3}	57.61	5.14	7.50	29.76
4	56.0×10^{-4}	29.06	2.56	3.26	65.12
5	97.0×10^{-4}	40.91	3.65	5.32	50.11
6	17.0×10^{-3}	25.10	0.93	1.35	72.62
7	21.0×10^{-4}	22.06	1.18	1.73	75.03
8	17.0×10^{-4}	18.75	1.01	1.47	78.78
9	22.0×10^{-4}	22.84	1.22	1.79	74.15
10	40.0×10^{-4}	34.28	1.84	2.68	61.20
11	25.0×10^{-4}	25.07	1.34	1.96	71.62
12	26.0×10^{-4}	25.78	1.38	2.02	70.82
13	58.0×10^{-4}	42.32	2.27	3.31	52.10
14	40.0×10^{-4}	34.28	1.84	2.68	61.20
15	43.0×10^{-4}	35.81	1.92	2.80	59.47
16	68.0×10^{-4}	45.83	2.46	3.58	48.13
17	28.0×10^{-4}	27.16	1.46	2.12	69.26
18	27.0×10^{-4}	26.48	1.42	2.07	70.03
19	37.0×10^{-4}	36.79	2.07	5.05	56.10
20	56.0×10^{-4}	41.54	2.23	3.25	52.98
21	30.0×10^{-4}	28.47	1.53	2.23	67.78
22	59.0×10^{-4}	38.05	1.94	1.70	58.30
23	41.0×10^{-4}	26.71	1.31	0.76	71.22
24	11.2×10^{-3}	46.06	2.21	0.98	50.72

APPENDIX C: LISTING OF COMPUTER CODE

```
      PROGRAM REACTOR
C DEVELOPED BY:  GRANT B. DUNCAN
C THESIS ADVISOR:  DR. R.M. COUNCE
C
C
C THIS FORTRAN CODE SIMULATES THE PERFORMANCE OF A BENCH-SCALE
C TRICKLE-BED BIOREACTOR USED TO COMETABOLIZE TRICHLOROETHYLENE AND
C TRANS-1,2-DICHLOROETHYLENE. THE BIOREACTOR WAS OPERATED IN CO-CURRENT
C DOWNWARD FLOW.  FOR DETAILED DESCRIPTION OF MODEL DEVELOPMENT, SEE
C USER'S MANUAL.  DEVELOPMENT OF THIS MODEL WAS MADE POSSIBLE THROUGH
C FUNDING PROVIDED BY THE OFFICE OF TECHNOLOGY DEVELOPMENT, U.S. DEPART-
C MENT OF ENERGY.  IT REMAINS THE PROPERTY OF SAID AGENCY AND ITS USE
C IS RESTRICTED.
C
C DEFINITION OF VARIABLES
C     LPRIME      LIQUID FLOW RATE, LITERS/MINUTE
C     L           LIQUID FLOW RATE, GRAMS/ CM^2 S
C     VL          LIQUID FLOW RATE, CM/S
C     GPRIME      GAS FLOW RATE, LITERS/MINUTE
C     G           GAS FLOW RATE, GRAM MOLS/ CM^2 S
C     VG          GAS FLOW RATE, CM/S
C     DLHCL       DIFFUSIVITY FOR HYDROCHLORIC ACID, CM^2/S
C     DLO2              "          "          OXYGEN,          "
C     DLCH4             "          "          METHANE,         "
C     DLCO2             "          "          CARBON DIOXIDE,  "
C     DLTCE             "          "          TRICHLOROETHYLENE,   "
C     DLDCE             "          "          DICHLOROETHYLENE,    "
C     SCHCL       SCHMIDT NUMBER FOR HYDROCHLORIC ACID
C     SCO2              "          "          "  OXYGEN
C     SCCH4             "          "          "  METHANE
C     SCCO2             "          "          "  CARBON DIOXIDE
C     SCTCE             "          "          "  TRICHLOROETHYLENE
C     SCDCE             "          "          "  DECHLOROETHYLENE
C     KLAHCL      LIQUID PHASE M.T. COEFFICIENT, HYDROCHLORIC ACID
C     KLAO2             "          "          "          "       , OXYGEN
C     KLACO2            "          "          "          "       , CARBON DIOXIDE
C     KLACH4            "          "          "          "       , METHANE
C     KLATCE            "          "          "          "       , TRICHLOROETHYLENE
C     KLADCE            "          "          "          "       , DICHLOROETHYLENE
C     KGAHCL      GAS   "          "          "          "       , HYDROCHLORIC ACID
C     KGA02             "          "          "          "       , OXYGEN
C     KGACO2            "          "          "          "       , CARBON DIOXIDE
C     KGACH4            "          "          "          "       , METHANE
C     KGATCE            "          "          "          "       , TRICHLOROETHYLENE
C     KGADCE            "          "          "          "       , DICHLOROETHYLENE
C     INVKYAHCL     GAS PHASE INTERMEDIATE M.T. COEFFICIENT, HCL
C     INVKYAO2          "          "          "          "          "       , O2
C     INVKYACO2         "          "          "          "          "       , CO2
C     INVKYACH4         "          "          "          "          "       , CH4
C     INVKYATCE         "          "          "          "          "       , TCE
C     INVKYADCE         "          "          "          "          "       , DCE
C     KYAHCL      OVERALL GAS-LIQUID M.T. COEFFICIENT, HYDROCHLORIC ACID
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C   KYAO2          "    "    "    "    "    , OXYGEN
C   KYACO2         "    "    "    "    "    , CARBON DIOXIDE
C   KYACH4         "    "    "    "    "    , METHANE
C   KYATCE         "    "    "    "    "    , TRICHLOROETHYLENE
C   KYADCE         "    "    "    "    "    , DICHLOROETHYLENE
C   KCHCL      LOCAL LIQUID-SOLID M.T. COEFFICIENT, HYDROCHLORIC ACID
C   KC02           "    "    "    "    "    , OXYGEN
C   KCCO2          "    "    "    "    "    , CARBON DIOXIDE
C   KCCH4          "    "    "    "    "    , METHANE
C   KCTCE          "    "    "    "    "    , TRICHLOROETHYLENE
C   KCDCE          "    "    "    "    "    , DICHLOROETHYLENE
C   INVKSAHCL  INTERMEDIATE LIQUID-SOLID M.T. COEFFICIENT, HCL
C   INVKSAO2       "    "    "    "    "    , O2
C   INVKSACO2      "    "    "    "    "    , CO2
C   INVKSACH4      "    "    "    "    "    , METHANE
C   INVKSATCE      "    "    "    "    "    , TCE
C   INVKSADCE      "    "    "    "    "    , DCE
C   KSAHCL     OVERALL LIQUID-SOLID M.T. COEFFICIENT, HYDROCHLORIC ACID
C   KSAO2          "    "    "    "    "    , OXYGEN
C   KSACO2         "    "    "    "    "    , CARBON DIOXIDE
C   KSACH4         "    "    "    "    "    , METHANE
C   KSATCE         "    "    "    "    "    , TRICHLOROETHYLENE
C   KSADCE         "    "    "    "    "    , DICHLOROETHYLENE
C   CHCL       CONCENTRATION TERM FOR USE IN GOVERNING EQUATIONS, HCL
C   CO2            "    "    "    "    "    "    "    "    , O2
C   CCO2           "    "    "    "    "    "    "    "    , CO2
C   CCH4           "    "    "    "    "    "    "    "    , CH4
C   CTCE           "    "    "    "    "    "    "    "    , TCE
C   CDCE           "    "    "    "    "    "    "    "    , DCE
C   MHCL       EQUILIBRIUM CONSTANT, HYDROCHLORIC ACID
C   MO2            "    "    , OXYGEN
C   MCO2           "    "    , CARBON DIOXIDE
C   MCH4           "    "    , METHANE
C   MTCE           "    "    , TRICHLOROETHYLENE
C   MDCE           "    "    , DICHOROETHYLENE
C   Y(1)       MOLE FRACTION HYDROCHLORIC ACID IN GAS PHASE
C   Y(2)       "    "  OXYGEN                    "    "    "
C   Y(3)       "    "  METHANE                   "    "    "
C   Y(4)       "    "  CARBON DIOXIDE            "    "    "
C   Y(5)       "    "  TRICHLOROETHYLENE         "    "    "
C   Y(6)       "    "  DICHLOROETHYLENE          "    "    "
C   Y(7)       "    "  HYDROCHLORIC ACID  IN LIQUID PHASE
C   Y(8)       "    "  OXYGEN                "    "    "
C   Y(9)       "    "  METHANE               "    "    "
C   Y(10)      "    "   CARBON DIOXIDE       "    "    "
C   Y(11)      "    "   TRICHLOROETHYLENE    "    "    "
C   Y(12)      "    "   DICHLOROETHYLENE     "    "    "
C   Y(13)      FOR MATERIAL BALANCES, MOLE FRACTION MUST SUM TO 1
C   Y(14)      "    "    "    ,    "    "    "    "    "    "
C   KSEC       REACTION RATE CONSTANT, SEC-1
C   KMIN         "    "    "  , MIN-1
C   VISC       VISCOSITY OF WATER, GRAMS/CM S
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C     RHO          DENSITY OF WATER, GRAMS/CM^3
C     PT           PRESSURE IN REACTOR, ATM
C     A1, A2, A3   INTERMEDIATE CALCULATED VALUES
C     COLHT        COLUMN HEIGHT IN CM
C     COLDI        COLUMN WIDTH IN CM
C     AP           SURFACE AREA OF PACKING
C     ALPHA        FRACTION OF PACKING COVERED WITH BIOMASS

C MAIN PROGRAM

      REAL*8 Y(14),t,tback,dt,tol
      REAL*8 LPRIME,L,VL,GPRIME,G,VG,DLHCL,DLO2,DLCH4,DLCO2,DLTCE,DLDCE,
     1VISC,RHO,PT,SCHCL,SCO2,SCCH4,SCCO2,SCTCE,SCDCE,KLAHCL,KLAO2,
     2KLACH4,KLACO2,KLATCE,KLADCE,MHCL,MO2,MCH4,MCO2,MTCE,MDCE,CHCL,CO2,
     3CCH4,CCO2,CTCE,CDCE,KGA,KGAHCL,KGAO2,KGACH4,KGACO2,KGATCE,KGADCE,
     4INVKYAHCL,INVKYAO2,INVKYACH4,INVKYACO2,INVKYATCE,INVKYADCE,KYAHCL,
     5KYAO2,KYACH4,KYACO2,KYATCE,KYADCE,DP,RHOP,ALPHA,RE,KCHCL,KCO2,
     6KCCH4,KCCO2,KCTCE,KCDCE,AC,INVKSAHCL,INVKSAO2,INVKSACH4,INVKSACO2,
     7INVKSATCE,INVKSADCE,KSAHCL,KSAO2,KSACH4,KSACO2,KSATCE,KSADCE,KSEC,
     8KMIN,NEWL,A1,A2,A3,AP,COLHT,COLDI
      REAL*8 GPERHCLGP,GPERHCLLP,GPERO2GP,GPERO2LP,GPERCH4GP,GPERCH4LP,
     1GPERCO2GP,GPERCO2LP,GPERTCGP,GPERTCELP,GPERDCEGP,GPERDCELP,
     2LPERHCLLP,LPERHCLSP,LPERO2LP,LPERO2SP,LPERCH4LP,LPERCH4SP,
     3LPERCO2LP,LPERCO2SP,LPERTCELP,LPERTCESP,LPERDCELP,LPERDCESP



      real*8 Z,Zout,I
      integer iwork
      real*8 rwork
      external der
      COMMON/PROP1/LPRIME,L,VL,GPRIME,G,VG,DLHCL,DLO2,DLCH4,DLCO2,DLTCE,
     1DLDCE,VISC,RHO,PT,SCHCL,SCO2,SCCH4,SCCO2,SCTCE,SCDCE,KLAHCL,KLAO2,
     2KLACH4,KLACO2,KLATCE,KLADCE,MHCL,MO2,MCH4,MCO2,MTCE,MDCE,CHCL,CO2,
     3CCH4,CCO2,CTCE,CDCE,KGA,KGAHCL,KGAO2,KGACH4,KGACO2,KGATCE,KGADCE,
     4INVKYAHCL,INVKYAO2,INVKYACH4,INVKYACO2,INVKYATCE,INVKYADCE,KYAHCL,
     5KYAO2,KYACH4,KYACO2,KYATCE,KYADCE,DP,RHOP,ALPHA,RE,KCHCL,KCO2,
     6KCCH4,KCCO2,KCTCE,KCDCE,AC,INVKSAHCL,INVKSAO2,INVKSACH4,INVKSACO2,
     7INVKSATCE,INVKSADCE,KSAHCL,KSAO2,KSACH4,KSACO2,KSATCE,KSADCE,KSEC,
     8KMIN,NEWL,A1,A2,A3,AP,COLHT,COLDI
       COMMON/PROP2/GPERHCLGP,GPERHCLLP,GPERO2GP,GPERO2LP,GPERCH4GP,
     1GPERCH4LP,GPERCO2GP,GPERCO2LP,GPERTCGP,GPERTCELP,GPERDCEGP,
     2GPERDCELP,LPERHCLLP,LPERHCLSP,LPERO2LP,LPERO2SP,LPERCH4LP,
     3LPERCH4SP,LPERCO2LP,LPERCO2SP,LPERTCELP,LPERTCESP,LPERDCELP,
     4LPERDCESP


* INITIALIZATION OF VARIABLES FOR ODE EQUATION SOLVER.
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C
C  INPUT OF THE LIQUID FLOW RATE IN LITERS/MINUTE
C
      CALL REFER

      WRITE(5,*) 'WHAT IS COLUMN HEIGHT IN CM'
      READ(5,*) COLHT

      WRITE(5,*) 'WHAT IS COLUMN DIAMETER IN CM'
      READ(5,*) COLDI

      WRITE(5,*) 'WHAT FRACTION OF PACKING COVERED WITH BIOMASS'
      READ(5,*) ALPHA

      WRITE(5,*) 'PLEASE ENTER THE LIQUID FLOW RATE IN LITERS/MINUTE'
      READ(5,*) LPRIME

      L = LPRIME*21.18044/(COLDI*COLDI)
      VL = LPRIME*21.2233/(COLDI*COLDI)
      NEWL = L/18.02

C  INPUT OF THE GAS FLOW RATE IN LITERS/MINUTE

      WRITE(5,*) 'PLEASE ENTER THE GAS FLOW RATE IN LITERS/MINUTE'
      READ(5,*) GPRIME

C****NOTE*** FOLLOWING CONVERSIONS ONLY VALID FOR 4% VOL/VOL METHANE
CONC.

      G = GPRIME*((1.2968/(60*28.489*.7853*(COLDI*COLDI))))
      VG = GPRIME*21.2233/(COLDI*COLDI)

C INPUT OF THE REACTION RATE CONSTANT IN 1/MIN
          WRITE(5,*) 'PLEASE ENTER THE REACTION RATE CONSTANT IN 1/MIN'
          READ(5,*) KMIN
          KSEC = KMIN/60
C INPUT OF INITIAL TCE CONCENTRATION
          WRITE(5,*) 'WHAT IS INITIAL CONCENTRATION OF TCE IN LIQ PHASE?'
          READ(5,*) A3

C  GENERATION OF MASS TRANSFER COEFFICIENTS FROM CORRELATIONS
C
C  LIQUID PHASE CORRELATION:  MAHAJANI AND SHARMA, CHEM ENGR SCIENCE,
C  34, 1429, 1979
C
C  LIQUID DIFFUSIVITIES SOURCE:  TREYBAL, PAGE 31, EQUATION 2.37
C  UNITS:  CM^2/S

      DLHCL = 1.9242E-05
      DLO2  = 2.839E-05
      DLCH4 = 1.873E-05
      DLCO2 = 1.873E-05
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```
      DLTCE = 8.658E-06
      DLDCE = 9.863E-06

C  VISCOSITY OF WATER;  MAIN COMPONENT OF LIQUID PHASE

      VISC =  9.82E-03

C  DENSITY OF WATER;  UNITS OF GRAMS/CM^3
      RHO =  .998

C  PRESSURE IN THE BIOREACTOR -- 1 ATM
      PT = 1


C  CALCULATION OF SCHMIDT NUMBER, A DIMENSIONLESS GROUP

      SCHCL = VISC/(RHO * DLHCL)
      SCO2  = VISC/(RHO * DLO2)
      SCCH4 = VISC/(RHO * DLCH4)
      SCCO2 = VISC/(RHO * DLCO2)
      SCTCE = VISC/(RHO * DLTCE)
      SCDCE = VISC/(RHO * DLDCE)


C  CALCULATION OF LIQUID PHASE MASS TRANSFER COEFFICIENTS
C  THE CORRELATION INCLUDES A TERM FOR THE INTERFACIAL AREA;  IT DOES
C  NOT HAVE TO BE CALCULATED SEPERATELY.

      KLAHCL =  8.08*((L/VISC)**.41)*(SCHCL**.5)*DLHCL
      KLAO2  =  8.08*((L/VISC)**.41)*(SCO2**.5)*DLO2
      KLACH4 =  8.08*((L/VISC)**.41)*(SCCH4**.5)*DLCH4
      KLACO2 =  8.08*((L/VISC)**.41)*(SCCO2**.5)*DLCO2
      KLATCE =  8.08*((L/VISC)**.41)*(SCTCE**.5)*DLTCE
      KLADCE =  8.08*((L/VISC)**.41)*(SCDCE**.5)*DLDCE

C  EQUILIBRIUM K VALUES FOR THE SIX COMPONENTS:

      MHCL =  10000
      MO2  =  41000
      MCH4 =  36400
      MCO2 =  31000
      MTCE =  186.6
      MDCE =  367


C  INITIAL CONCENTRATION OF SIX COMPONENTS:

      CHCL =  .0554
      CO2  =  .0554
      CCH4 =  .0554
      CCO2 =  .0554
      CTCE =  .0554
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```
      CDCE =  .0554

C  GAS PHASE CORRELATION:  SHENDE AND SHARMA, CHEM ENGR SCIENCE, 29,
C  1429, 1763, 1974.

      KGA = 0.610E-05*(VG**.866)*(VL**.340)

      KGAHCL = KGA
      KGAO2  = KGA
      KGACH4 = KGA
      KGACO2 = KGA
      KGATCE = KGA
      KGADCE = KGA

C  OVERALL MASS TRANSFER COEFFICIENT--BASED ON GAS PHASE

          INVKYAHCL = 1/(KGAHCL*PT) + MHCL/(KLAHCL*CHCL)
          INVKYAO2  = 1/(KGAO2*PT) + MO2/(KLAO2*CO2)
          INVKYACH4 = 1/(KGACH4*PT) + MCH4/(KLACH4*CCH4)
          INVKYACO2 = 1/(KGACO2*PT) + MCO2/(KLACO2*CCO2)
          INVKYATCE = 1/(KGATCE*PT) + MTCE/(KLATCE*CTCE)
          INVKYADCE = 1/(KGADCE*PT) + MDCE/(KLADCE*CDCE)

C CALCULATION OF RELATIVE CONTRIBUTIONS TO OVERALL MASS TRANSFER BASED
C ON GAS PHASE

          GPERHCLGP = ((1/(KGAHCL*PT))/INVKYAHCL)*100
          GPERHCLLP = ((MHCL/(KLAHCL*CHCL))/INVKYAHCL)*100

          GPERO2GP = ((1/(KGAO2*PT))/INVKYAO2)*100
          GPERO2LP = ((MO2/(KLAO2*CO2))/INVKYAO2)*100

          GPERCH4GP = ((1/(KGACH4*PT))/INVKYACH4)*100
          GPERCH4LP = ((MCH4/(KLACH4*CCH4))/INVKYACH4)*100

          GPERCO2GP = ((1/(KGACO2*PT))/INVKYACO2)*100
          GPERCO2LP = ((MCO2/(KLACO2*CCO2))/INVKYACO2)*100

          GPERTCGP = ((1/(KGATCE*PT))/INVKYATCE)*100
          GPERTCELP = ((MTCE/(KLATCE*CTCE))/INVKYATCE)*100

          GPERDCEGP = ((1/(KGADCE*PT))/INVKYADCE)*100
          GPERDCELP = ((MDCE/(KLADCE*CDCE))/INVKYADCE)*100


          KYAHCL = 1/INVKYAHCL
          KYAO2  = 1/INVKYAO2
          KYACH4 = 1/INVKYACH4
          KYACO2 = 1/INVKYACO2
          KYATCE = 1/INVKYATCE
          KYADCE = 1/INVKYADCE
```

```
C  CALCULATION OF LIQUID-SOLID MASS TRANSFER COEFFICIENT

C  DP IS THE DIAMETER OF THE PACKING
       DP = .6

C  RHOP IS THE DENSITY OF THE PACKING IN GRAMS/CM^3
       RHOP = .9

C  RE IS THE LIQUID REYNOLDS NUMBER
       RE = (L*DP)/VISC

       KCHCL = DLHCL/(DP*ALPHA)*((.266*(RE**1.15))*(SCHCL**.3333333))
       KCO2  = DLO2/(DP*ALPHA)*((.266*(RE**1.15))*(SCO2**.3333333))
       KCCH4 = DLCH4/(DP*ALPHA)*((.266*(RE**1.15))*(SCCH4**.3333333))
       KCCO2 = DLCO2/(DP*ALPHA)*((.266*(RE**1.15))*(SCCO2**.3333333))
       KCTCE = DLTCE/(DP*ALPHA)*((.266*(RE**1.15))*(SCTCE**.3333333))
       KCDCE = DLDCE/(DP*ALPHA)*((.266*(RE**1.15))*(SCDCE**.3333333))

       AP  = 8.9999

C  CALCULATION OF THE OVERALL LIQUID-SOLID MASS TRANSFER COEFFICIENT


       INVKSAHCL = 1/(KCHCL*AP) + 1/KSEC
       INVKSAO2  = 1/(KCO2*AP) + 1/KSEC
       INVKSACH4 = 1/(KCCH4*AP) + 1/KSEC
       INVKSACO2 = 1/(KCCO2*AP) + 1/KSEC
       INVKSATCE = 1/(KCTCE*AP) + 1/KSEC
       INVKSADCE = 1/(KCDCE*AP) + 1/KSEC


C CALCULATION OF RELATIVE CONTRIBUTIONS TO OVERALL MASS TRANSFER BASED
C ON LIQUID PHASE

       LPERHCLLP = ((1/(KCHCL*AP))/INVKSAHCL)*100
       LPERHCLSP = ((1/KSEC)/INVKSAHCL)*100

       LPERO2LP = ((1/(KCO2*AP))/INVKSA02)*100
       LPERO2SP = ((1/KSEC)/INVKSAO2)*100

       LPERCH4LP = ((1/(KCCH4*AP))/INVKSACH4)*100
       LPERCH4SP = ((1/KSEC)/INVKSACH4)*100

       LPERCO2LP = ((1/(KCCO2*AP))/INVKSACO2)*100
       LPERCO2SP = ((1/KSEC)/INVKSACO2)*100

       LPERTCELP = ((1/(KCTCE*AP))/INVKSATCE)*100
       LPERTCESP = ((1/KSEC)/INVKSATCE)*100

       LPERDCELP = ((1/(KCDCE*AP))/INVKSADCE)*100
       LPERDCESP = ((1/KSEC)/INVKSADCE)*100
```

```
      KSAHCL = (1/INVKSAHCL)
      KSAO2  = (1/INVKSAO2)
      KSACH4 = (1/INVKSACH4)
      KSACO2 = (1/INVKSACO2)
      KSATCE = (1/INVKSATCE)
      KSADCE = (1/INVKSADCE)

C  CALLING OF SUBROUTINE AND SOLVING OF EQUATION

      iout=26
      OPEN (iout, FILE = 'OUTPUT', STATUS = 'NEW')

***  THIS IS THE INITIALIZATION NEEDED BEFORE ANY INTEGRATION

      Z = 0.0
C  THE TWELVE INITIAL CONDITIONS

C  GAS PHASE
C
      WRITE(5,*) 'INITIAL HYDROCHLORIC ACID MOLE FRACTION IN GAS PHASE'
      READ(5,*) Y(1)

      WRITE(5,*) 'INITIAL OXYGEN MOLE FRACTION IN GAS PHASE'
      READ(5,*) Y(2)

      WRITE(5,*) 'INITIAL METHANE MOLE FRACTION IN GAS PHASE'
      READ(5,*) Y(3)

      WRITE(5,*) 'INITIAL CARBON DIOXIDE MOLE FRACTION IN GAS PHASE'
      READ(5,*) Y(4)

      WRITE(5,*) 'INITIAL TRICHLOROETHYLENE MOLE FRACTION IN GAS PHASE'
      READ(5,*) Y(5)

      WRITE(5,*) 'INITIAL DICHLOROETHYLENE MOLE FRACTION IN GAS PHASE'
      READ(5,*) Y(6)

C  LIQUID PHASE

      WRITE(5,*) 'INITIAL HYDROCHLORIC ACID MOLE FRACTION IN LIQUID PHASE'
      READ(5,*) Y(7)

      WRITE(5,*) 'INITIAL OXYGEN MOLE FRACTION IN LIQUID PHASE'
      READ(5,*) Y(8)

      WRITE(5,*) 'INITIAL METHANE MOLE FRACTION IN LIQUID PHASE'
      READ(5,*) Y(9)

      WRITE(5,*) 'INITIAL CARBON DIOXIDE MOLE FRACTION IN LIQUID PHASE'
      READ(5,*) Y(10)
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      WRITE(5,*) 'INITIAL TRICHLOROETHYLENE MOLE FRACTION IN LIQUID PHASE'
      READ(5,*) Y(11)

      WRITE(5,*) 'INITIAL DICHLOROETHYLENE MOLE FRACTION IN LIQUID PHASE'
      READ(5,*) Y(12)

      Y(13) = 1 - Y(1) - Y(2) - Y(3) - Y(4) - Y(5) - Y(6)
      Y(14) = 1 - Y(7) - Y(8) - Y(9) - Y(10) - Y(11) - Y(12)
   NEQ=14
   ISTATE=1
      WRITE(IOUT,905) LPRIME
905   FORMAT(/,X,'LIQUID FLOW RATE:',F10.4,' LITERS/MINUTE')
      WRITE(IOUT,906) GPRIME
906   FORMAT(/,X,'GAS FLOW RATE:',F10.4,' LITERS/MINUTE')
      WRITE(IOUT,*)
      WRITE(IOUT,910)
910   FORMAT(
  1'  HCL      O2       CH4      CO2      TCE      DCE'
  1,//)
      WRITE(IOUT,920)Z
      WRITE(IOUT,930)(Y(K5),K5 = 1, 12)
   DO 100 I = 10, COLHT, 10
C    WANT TO START AT ENTRANCE OF COLUMN AND PROCEED DOWN THE COLUMN IN
C    10.0 CM INCREMENTS
C
      Zout = DBLE(I)
      tol = 1e-10
      dt = (zout - z)*0.0001
      call rk(z,zout,tol,y,neq,dt,tback,der)
      Z=Zout

      WRITE(IOUT,920)Z
      WRITE(IOUT,930)(Y(K5),K5 = 1, 12)
920   FORMAT(/,X,' AT Z = ',F5.1,' CM ')
930   FORMAT(6(X,E10.3),/,6(X,E10.3))
100   continue

*** THIS IS THE END OF THE INTEGRATION

      A1  = ((A3 - Y(11))/A3)*100
      A2  = (((A3 - Y(11))/A3) - (((G/NEWL)*Y(5))/A3))*100

      WRITE(IOUT,940) A1
940   FORMAT(/,X,'PERCENT REMOVED FROM LIQUID PHASE: ',F6.3)
      WRITE(IOUT,950) A2
950   FORMAT(/,X,'PERCENT DESTROYED BY BIOMASS ACTIVITY: ',F6.3)
      WRITE(IOUT,960) KMIN
960   FORMAT(/,X,'REACTION RATE CONSTANT (MIN-1): ',E10.3)

      WRITE(IOUT,*)
      WRITE(IOUT,*)
```

```
      WRITE(IOUT,961) GPERHCLGP
961   FORMAT(/,X,'RESISTANCE DUE TO KGA FOR HCL: ',F6.3)
      WRITE(IOUT,962) GPERHCLLP
962   FORMAT(/,X,'RESISTANCE DUE TO KLA FOR HCL: ',F6.3)
      WRITE(IOUT,*)

      WRITE(IOUT,963) GPERO2GP
963   FORMAT(/,X,'RESISTANCE DUE TO KGA FOR O2: ',F6.3)
      WRITE(IOUT,964) GPERO2LP
964   FORMAT(/,X,'RESISTANCE DUE TO KLA FOR O2: ',F6.3)
      WRITE(IOUT,*)


      WRITE(IOUT,965) GPERCH4GP
965   FORMAT(/,X,'RESISTANCE DUE TO KGA FOR CH4: ',F6.3)
      WRITE(IOUT,966) GPERCH4LP
966   FORMAT(/,X,'RESISTANCE DUE TO KLA FOR CH4: ',F6.3)
      WRITE(IOUT,*)


      WRITE(IOUT,967) GPERCO2GP
967   FORMAT(/,X,'RESISTANCE DUE TO KGA FOR CO2: ',F6.3)
      WRITE(IOUT,968) GPERCO2LP
968   FORMAT(/,X,'RESISTANCE DUE TO KLA FOR CO2: ',F6.3)
      WRITE(IOUT,*)


      WRITE(IOUT,969) GPERTCGP
969   FORMAT(/,X,'RESISTANCE DUE TO KGA FOR TCE: ',F6.3)
      WRITE(IOUT,970) GPERTCELP
970   FORMAT(/,X,'RESISTANCE DUE TO KLA FOR TCE: ',F6.3)
      WRITE(IOUT,*)


      WRITE(IOUT,971) GPERDCEGP
971   FORMAT(/,X,'RESISTANCE DUE TO KGA FOR DCE: ',F6.3)
      WRITE(IOUT,972) GPERDCELP
972   FORMAT(/,X,'RESISTANCE DUE TO KLA FOR DCE: ',F6.3)
      WRITE(IOUT,*)
      WRITE(IOUT,*)
      WRITE(IOUT,*)


      WRITE(IOUT,973) LPERHCLLP
973   FORMAT(/,X,'RESISTANCE DUE TO KSA FOR HCL: ',F6.3)
      WRITE(IOUT,974) LPERHCLSP
974   FORMAT(/,X,'RESISTANCE DUE TO K FOR HCL: ',F6.3)
      WRITE(IOUT,*)


      WRITE(IOUT,975) LPERO2LP
975   FORMAT(/,X,'RESISTANCE DUE TO KSA FOR O2: ',F6.3)
```

```
      WRITE(IOUT,976) LPERO2SP
976   FORMAT(/,X,'RESISTANCE DUE TO K FOR O2: ',F6.3)
      WRITE(IOUT,*)


      WRITE(IOUT,977) LPERCH4LP
977   FORMAT(/,X,'RESISTANCE DUE TO KSA FOR CH4: ',F6.3)
      WRITE(IOUT,978) LPERCH4SP
978   FORMAT(/,X,'RESISTANCE DUE TO K FOR CH4: ',F6.3)
      WRITE(IOUT,*)


      WRITE(IOUT,979) LPERCO2LP
979   FORMAT(/,X,'RESISTANCE DUE TO KSA FOR CO2: ',F6.3)
      WRITE(IOUT,980) LPERCO2SP
980   FORMAT(/,X,'RESISTANCE DUE TO K FOR CO2: ',F6.3)
      WRITE(IOUT,*)


      WRITE(IOUT,981) LPERTCELP
981   FORMAT(/,X,'RESISTANCE DUE TO KSA FOR TCE: ',F6.3)
      WRITE(IOUT,982) LPERTCESP
982   FORMAT(/,X,'RESISTANCE DUE TO K FOR TCE: ',F6.3)
      WRITE(IOUT,*)


      WRITE(IOUT,983) LPERDCELP
983   FORMAT(/,X,'RESISTANCE DUE TO KSA FOR DCE: ',F6.3)
      WRITE(IOUT,984) LPERDCESP
984   FORMAT(/,X,'RESISTANCE DUE TO K FOR DCE: ',F6.3)

    STOP
    END

C   SUBROUTINE RK
C
C   PURPOSE
C     SOLUTION OF FIRST ORDER O.D.E., INITIAL VALUE PROBLEM,
C     BY SEVENTH ORDER RUNGE-KUTTA INTEGRATION WITH STEPSIZE
C     CONTROL
C
C   USAGE
C     CALL RK(TI,TF,TOL,P,N,DT,T,DER)
C
C   DESCRIPTION OF PARAMETERS
C     TI  - INITIAL VALUE OF THE INDEP. VARIABLE (INPUT)
C     TF  - FINAL VALUE OF THE INDEP. VARIABLE (INPUT)
C     TOL  - TOLERANCE OR ALLOWABLE SIZE OF ERRORS IN P
C          (INPUT)
C     P   - INITIAL VALUE ARRAY OF THE DEP. VARIABLES (INPUT)
C          P ARRAY IS ALTERED BY RK SO THAT VALUE OF P
C          AFTER CALL IS THE VALUE OF P AT T=TF
```

```
C     N   - NUMBER OF ELEMENTS IN P ARRAY (INPUT)
C     DT  - FIRST ESTIMATE OF STEPSIZE (INPUT)
C     T   - VALUE OF INDEPENDANT VARIABLE AT TIME OF PROGRAM
C           SHUT-OFF (OUTPUT)
C     DER - NAME OF DERIVATIVE SUBPROGRAM USED (INPUT)
C
C   METHOD
C     METHOD IS DESCRIBED IN NASA TR R-287
C     (BY E. FEHLBERG)
C
C   REMARKS
C     SUBSCRIPTS FOR ALPHA, BETA, AND CH ARE +1 GREATER THAN
C     USED BY FEHLBERG
C     F(I) IS F(I+1,J)
C
C   SUBPROGRAMS REQUIRED
C     SUBROUTINE REFER HAS TO BE CALLED ONCE AT THE BEGINNING
C     OF THE CALLING PROGRAM.
C     SUBROUTINE DER(P,T,F) HAS TO BE PROVIDED
C     WHERE  DP/DT = F(P,T)
C     USER SUPPLIED SUBROUTINE
C           PRIN(T,P,I) IS CALLED AT THE START (WITH I=1)
C           AND AT THE END OF EACH STEP (WITH I=0) SO
C           THAT USER CAN PRINT INTERMEDIATE RESULTS
C
C
      SUBROUTINE RK (TI,TF,TOL,P,N,DT,T,DER)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/FELCON/ CH(13),ALPH(13),BETA(13,12)
      DIMENSION F(13,90),XDUM(90),TE(90),P(N)
      TOL10=TOL*0.1D0
      T=TI
      CALL DER(P,T,TE)
   10 CONTINUE
      CALL DER(P,T,TE)
      DO 20 I=1,N
   20 F(1,I)=TE(I)
   30 CONTINUE
      DO 50 K=2,13
      DO 60 I=1,N
   60 XDUM(I)=P(I)
      NN=K-1
      DO 70 I=1,N
      DO 70 J=1,NN
   70 XDUM(I)=XDUM(I)+DT*BETA(K,J)*F(J,I)
      TDUM=T+ALPH(K)*DT
      CALL DER(XDUM,TDUM,TE)
      DO 80 I=1,N
   80 F(K,I)=TE(I)
   50 CONTINUE
      DO 90 I=1,N
   90 XDUM(I)=P(I)
```

```
      DO 100 I=1,N
      DO 100 L=1,13
  100 P(I)=P(I)+DT*CH(L)*F(L,I)
      ER=1.0D-30
      DO 110 I=1,N
      TE(I)=DT*(F(1,I)+F(11,I)-F(12,I)-F(13,I))*41.0D0/840.0D0
  110 ER=TE(I)*TE(I)+ER
      ER=SQRT(ER)
      DT1=DT
      DT=DT1*(TOL10/ER)**0.125D0
      IF (ER-TOL) 120,120,130
  120 T=T+DT1
      IF(ABS(T-TF).LT.1.0D-13) GO TO 190
      IF(DT) 123,122,122
  122 IF(TF-(T+DT))124,124,126
  123 IF(TF-(T+DT))126,124,124
  124 DT=TF-T
  126 CONTINUE
C     TOLERANCE IS PASSED
      GO TO 10
  130 DO 140 I=1,N
  140 P(I)=XDUM(I)
      GO TO 30
  190 CONTINUE
      CALL DER(P,T,TE)
      RETURN
      END
      SUBROUTINE REFER
C
C     COEFFICIENTS FOR SEVENTH ORDER RUNGE-KUTTA SCHEME AS GIVEN
C     IN NASA TR R-287 P.65 TABLE X
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/FELCON/ CH(13),ALPH(13),BETA(13,12)
      DO 10 I=1,13
      DO 20 J=1,12
   20 BETA(I,J)=0.0D0
      ALPH(I)=0.0D0
   10 CH(I)=0.0D0
      CH(6)=34.0D0/105.0D0
      CH(7)=9.0D0/35.0D0
      CH(8)=CH(7)
      CH(9)=9.0D0/280.0D0
      CH(10)=CH(9)
      CH(12)=41.0D0/840.0D0
      CH(13)=CH(12)
      ALPH(2)=2.0D0/27.0D0
      ALPH(3)=1.0D0/9.0D0
      ALPH(4)=1.0D0/6.0D0
      ALPH(5)=5.0D0/12.0D0
      ALPH(6)=0.5D0
      ALPH(7)=5.0D0/6.0D0
```

```
ALPH(8)=1.0D0/6.0D0
ALPH(9)=2.0D0/3.0D0
ALPH(10)=1.0D0/3.0D0
ALPH(11)=1.0D0
ALPH(13)=1.0D0
BETA(2,1)=2.0D0/27.0D0
BETA(3,1)=1.0D0/36.0D0
BETA(4,1)=1.0D0/24.0D0
BETA(5,1)=5.0D0/12.0D0
BETA(6,1)=1.0D0/20.0D0
BETA(7,1)=-25.0D0/108.0D0
BETA(8,1)=31.0D0/300.0D0
BETA(9,1)=2.0D0
BETA(10,1)=-91.0D0/108.0D0
BETA(11,1)=2383.0D0/4100.0D0
BETA(12,1)=3.0D0/205.0D0
BETA(13,1)=-1777.0D0/4100.0D0
BETA(3,2)=1.0D0/12.0D0
BETA(4,3)=1.0D0/8.0D0
BETA(5,3)=-25.0D0/16.0D0
BETA(5,4)=-BETA(5,3)
BETA(6,4)=1.0D0/4.0D0
BETA(7,4)=125.0D0/108.0D0
BETA(9,4)=-53.0D0/6.0D0
BETA(10,4)=23.0D0/108.0D0
BETA(11,4)=-341.0D0/164.0D0
BETA(13,4)=BETA(11,4)
BETA(6,5)=1.0D0/5.0D0
BETA(7,5)=-65.0D0/27.0D0
BETA(8,5)=61.0D0/225.0D0
BETA(9,5)=704.0D0/45.0D0
BETA(10,5)=-976.0D0/135.0D0
BETA(11,5)=4496.0D0/1025.0D0
BETA(13,5)=BETA(11,5)
BETA(7,6)=125.0D0/54.0D0
BETA(8,6)=-2.0D0/9.0D0
BETA(9,6)=-107.0D0/9.0D0
BETA(10,6)=311.0D0/54.0D0
BETA(11,6)=-301.0D0/82.0D0
BETA(12,6)=-6.0D0/41.0D0
BETA(13,6)=-289.0D0/82.0D0
BETA(8,7)=13.0D0/900.0D0
BETA(9,7)=67.0D0/90.0D0
BETA(10,7)=-19.0D0/60.0D0
BETA(11,7)=2133.0D0/4100.0D0
BETA(12,7)=-3.0D0/205.0D0
BETA(13,7)=2193.0D0/4100.0D0
BETA(9,8)=3.0D0
BETA(10,8)=17.0D0/6.0D0
BETA(11,8)=45.0D0/82.0D0
BETA(12,8)=-3.0D0/41.0D0
BETA(13,8)=51.0D0/82.0D0
```

```
      BETA(10,9)=-1.0D0/12.0D0
      BETA(11,9)=45.0D0/164.0D0
      BETA(12,9)=3.0D0/41.0D0
      BETA(13,9)=33.0D0/164.0D0
      BETA(11,10)=18.0D0/41.0D0
      BETA(12,10)=6.0D0/41.0D0
      BETA(13,10)=12.0D0/41.0D0
      BETA(13,12)=1.0D0
      RETURN
      END
C
C  THE FOLLOWING IS THE SUBROUTINE NAMED DER WHICH CONTAINS THE 12
C  GOVERNING EQUATIONS FOR THE MODEL.  THE SUBROUTINE ALLOWS THE VARIOUS
C  PROPERTIES TO BE INTEGRATED INTO THE GOVERNING EQUATIONS.
C
      SUBROUTINE DER(Y, t, YP)
      REAL*8 Z,Y,YP,t
      DIMENSION Y(14), YP(14)
c
      REAL*8 LPRIME,L,VL,GPRIME,G,VG,DLHCL,DLO2,DLCH4,DLCO2,DLTCE,DLDCE,
     1VISC,RHO,PT,SCHCL,SCO2,SCCH4,SCCO2,SCTCE,SCDCE,KLAHCL,KLAO2,
     2KLACH4,KLACO2,KLATCE,KLADCE,MHCL,MO2,MCH4,MCO2,MTCE,MDCE,CHCL,CO2,
     3CCH4,CCO2,CTCE,CDCE,KGA,KGAHCL,KGAO2,KGACH4,KGACO2,KGATCE,KGADCE,
     4INVKYAHCL,INVKYAO2,INVKYACH4,INVKYACO2,INVKYATCE,INVKYADCE,KYAHCL,
     5KYAO2,KYACH4,KYACO2,KYATCE,KYADCE,DP,RHOP,ALPHA,RE,KCHCL,KCO2,
     6KCCH4,KCCO2,KCTCE,KCDCE,AC,INVKSAHCL,INVKSAO2,INVKSACH4,INVKSACO2,
     7INVKSATCE,INVKSADCE,KSAHCL,KSAO2,KSACH4,KSACO2,KSATCE,KSADCE,KSEC,
     8KMIN,NEWL,A1,A2,A3,AP,COLHT,COLDI
      REAL*8 GPERHCLGP,GPERHCLLP,GPERO2GP,GPERO2LP,GPERCH4GP,
     1GPERCH4LP,GPERCO2GP,GPERCO2LP,GPERTCGP,GPERTCELP,GPERDCEGP,
     2GPERDCELP,LPERHCLLP,LPERHCLSP,LPERO2LP,LPERO2SP,LPERCH4LP,
     3LPERCH4SP,LPERCO2LP,LPERCO2SP,LPERTCELP,LPERTCESP,LPERDCELP,
     4LPERDCESP



      COMMON/PROP1/LPRIME,L,VL,GPRIME,G,VG,DLHCL,DLO2,DLCH4,DLCO2,DLTCE,
     1DLDCE,VISC,RHO,PT,SCHCL,SCO2,SCCH4,SCCO2,SCTCE,SCDCE,KLAHCL,KLAO2,
     2KLACH4,KLACO2,KLATCE,KLADCE,MHCL,MO2,MCH4,MCO2,MTCE,MDCE,CHCL,CO2,
     3CCH4,CCO2,CTCE,CDCE,KGA,KGAHCL,KGAO2,KGACH4,KGACO2,KGATCE,KGADCE,
     4INVKYAHCL,INVKYAO2,INVKYACH4,INVKYACO2,INVKYATCE,INVKYADCE,KYAHCL,
     5KYAO2,KYACH4,KYACO2,KYATCE,KYADCE,DP,RHOP,ALPHA,RE,KCHCL,KCO2,
     6KCCH4,KCCO2,KCTCE,KCDCE,AC,INVKSAHCL,INVKSAO2,INVKSACH4,INVKSACO2,
     7INVKSATCE,INVKSADCE,KSAHCL,KSAO2,KSACH4,KSACO2,KSATCE,KSADCE,KSEC,
     8KMIN,NEWL,A1,A2,A3,AP,COLHT,COLDI
      COMMON/PROP2/GPERHCLGP,GPERHCLLP,GPERO2GP,GPERO2LP,GPERCH4GP,
     1GPERCH4LP,GPERCO2GP,GPERCO2LP,GPERTCGP,GPERTCELP,GPERDCEGP,
     2GPERDCELP,LPERHCLLP,LPERHCLSP,LPERO2LP,LPERO2SP,LPERCH4LP,
     3LPERCH4SP,LPERCO2LP,LPERCO2SP,LPERTCELP,LPERTCESP,LPERDCELP,
     4LPERDCESP
```

```
C  THE TWELVE GOVERNING EQUATIONS:

C  GAS PHASE

      YP(1)  =  -((KYAHCL)/G)*(Y(1) - MHCL*Y(7))
      YP(2)  =  -((KYAO2)/G)*(Y(2) - MO2*Y(8))
      YP(3)  =  -((KYACH4)/G)*(Y(3) - MCH4*Y(9))
      YP(4)  =  -((KYACO2)/G)*(Y(4) - MCO2*Y(10))
      YP(5)  =  -((KYATCE)/G)*(Y(5) - MTCE*Y(11))
      YP(6)  =  -((KYADCE)/G)*(Y(6) - MDCE*Y(12))

C  LIQUID PHASE

      YP(7)  =  -((KSAHCL*CHCL)/NEWL)*Y(7) +
     1          ((KYAHCL)/NEWL)*(Y(1) - MHCL*Y(7))

      YP(8)  =  -((KSAO2*CO2)/NEWL)*Y(8)  +
     1          ((KYAO2)/NEWL)*(Y(2) - MO2*Y(8))

      YP(9)  =  -((KSACH4*CCH4)/NEWL)*Y(9) +
     1          ((KYACH4)/NEWL)*(Y(3) - MCH4*Y(9))

      YP(10) =  -((KSACO2*CCO2)/NEWL)*Y(10) +
     1          ((KYACO2)/NEWL)*(Y(4) - MCO2*Y(10))

      YP(11) =  -((KSATCE*CTCE)/NEWL)*Y(11) +
     1          ((KYATCE)/NEWL)*(Y(5) - MTCE*Y(11))

      YP(12) =  -((KSADCE*CDCE)/NEWL)*Y(12) +
     1          ((KYADCE)/NEWL)*(Y(6) - MDCE*Y(12))


      YP(13) = - YP(1) - YP(2) - YP(3) - YP(4) - YP(5) - YP(6)
      YP(14) = - YP(7) - YP(8) - YP(9) - YP(10) - YP(11) - YP(12)


      iout=6

      RETURN
      END
```

VITA

Grant Berkley Duncan was born in Waverly, Tennessee on March 23, 1963. He attended elementary and junior high schools in Waverly and graduated from Waverly Central High School in May, 1981. The following September he entered The University of Tennessee, Martin, majoring in chemical engineering. In September, 1983 he transferred to The University of Tennessee, Knoxville, and received a Bachelor of Science in Chemical Engineering in March, 1988. In January, 1989 he reentered The University of Tennessee, Knoxville, and in December, 1994 received a Master of Science degree in Chemical Engineering.

Since April, 1991 he has been employed by The B.F.Goodrich Company in Calvert City, Kentucky as a Process Engineer in the Chlor-Alkali and Olefins Division's Ethylene Department. He and his wife Laura and son Reece reside in Paducah, Kentucky.