$$\text{moles } H^{+} = 0.005 + \text{moles } CH_3COOH = \text{moles NaOH added}$$

The above relation can easily be solved for the number of moles of acetic acid. The concentration of acetic acid in the original (sampled) solution can now be calculated as follows:

$$[CH_3COOH] = \frac{\text{moles } CH_3COOH}{V_{\text{sample}}} = \frac{\text{moles NaOH added} - 0.005}{V_{\text{sample}}}$$

$$= \frac{0.1V_{NaOH} - 0.005}{V_{\text{sample}}} \qquad \ldots(III/2)$$

Eqn.(III/2) is the desired result.

III.2 - Chromatographic Calibrations

Janik (1980) has shown that the accuracy of chromatographic calibration on the basis of peak height is of the same order as that based on 'peak-height times peak width at ½ height'. Thus, since electronic integrators are costly and not warranted in this case, calibration was done on the basis of peak-height.

The high-pressure liquid-chromatograph (HPLC) was calibrated before each run, since small variations in temperature of the apparatus and in mobile-phase concentration introduced appreciable errors. Variations in successive calibration curves were small; sample calibration data are shown in Table III.1 below.

Table III.1

Sample HPLC Calibration Data

Acetic Acid Peak Height [mm]	Acetic Acid Concentration [g/l]	Furfural Peak Height [mm]	Furfural Concentration [g/l]
19	1.05	8	0.116
38	2.10	17	0.289
71	4.20	31	0.578
102	6.30	47	1.156
		55	2.312
		57.5	3.468

Detector - Acetic acid : conductivity, signal attenuation = 2
- Furfural : ultraviolet, signal attenuation = 4

Mobile phase - 1 mM pthalic acid, pH=3.8. Flowrate = 2 ml/min.

Chart range = 0 - 200 mV for both detectors

The figures in Table III.1 are plotted in Fig.5.1, from which it is clear that for this particular calibration, furfural determinations are most accurate at concentrations below 2g/l. Samples with higher concentrations should thus be diluted to ensure that determination is done within this range. The acetic acid calibration is quite linear, and accuracy is independent of concentration in the range calibrated.

APPENDIX IV - Mass-transfer Parameter Estimation

The experimental measurements on stirred-tank batch adsorbers are summarised below. Experimental conditions and quantities are noted. Two runs for each combination of solute and adsorbent were done.

IV.1 Adsorption onto CS-10

Raw data are summarised in Tables IV.1 and IV.2 below.

Table IV.1

CS-10 Stirred-tank Batch Adsorber Runs

Adsorption of Acetic Acid

Run 1		Run 2	
W_s=300 g		W_s=300 g	
V_l=7 l		V_l=7 l	
C_o=6.86 g/l		C_o=3.55 g/l	
C [g/l]	t [min]	C [g/l]	t [min]
5.00	2.50	1.48	2.5
4.52	5.50	0.84	5.5
3.86	10.25	0.58	10.33
3.71	21.50	0.18	21.6
3.52	33.75	0.16	39.0
3.46	54.00		

Table IV.2

CS-10 Stirred-tank Batch Adsorber Runs

Adsorption of Furfural

Run 1		Run 2	
W_s=140 g		W_s=200 g	
V_l=7 l		V_l=7 l	
C_o=6.26 g/l		C_o=2.92 g/l	
C [g/l]	t [min]	C [g/l]	t [min]
4.39	3.00	2.19	2.50
3.86	7.00	2.07	5.50
3.67	10.50	1.89	9.50
3.58	15.50	1.55	21.75
3.56	21.50	1.24	35.75
3.46	37.50	1.00	68.00
3.20	71.00	0.74	97.00
2.89	100.00	0.51	135.00
2.52	210.00	0.28	180.00

IV.2 Adsorption onto CS-15

Raw data are summarised in Tables IV.3 and IV.4 below.

Table IV.3

CS-15 Stirred-tank Batch Adsorber Runs

Adsorption of Acetic Acid

Run 1		Run 2	
W_s=210 g		W_s=300 g	
V_l=7 l		V_l=7 l	
C_o=5.21 g/l		C_o=3.19 g/l	
C [g/l]	t [min]	C [g/l]	t [min]
2.67	5.00	1.18	2.00
2.47	11.00	0.86	4.50
2.33	16.50	0.71	9.33
2.33	22.00	0.73	16.5

Table IV.4

CS-15 Stirred-tank Batch Adsorber Runs

Adsorption of Furfural

Run 1		Run 2	
$W_s=110$ g		$W_s=200$ g	
$V_l=7$ l		$V_l=7$ l	
$C_o=6.29$ g/l		$C_o=2.96$ g/l	
C [g/l]	t [min]	C [g/l]	t [min]
4.17	2.25	1.92	2.50
3.81	5.13	1.73	5.50
3.68	10.25	1.31	12.25
3.59	15.75	0.98	20.50
3.46	23.00	0.75	30.00
3.21	40.50	0.64	53.25
2.88	63.00	0.55	79.00
2.65	90.00	0.26	188.00

The figures in Tables IV.1 to IV.4 are plotted in Figs. 4.1 to 4.4.

IV.3 Sample Calculation of Mass-transfer Coefficient in a Fluidised-bed

The liquid-side mass-transfer coefficient in the bed of fluidised adsorbent was estimated from the following correlation given by Kunii and Levenspiel (1969):

$$Sh = 2 + 1.5\ Sc^{0.33}[(1-\epsilon_b)Re]^{½}$$

The molecular diffusivity of furfural in water at 25°C was estimated from data and equations presented by Treybal (1980) to be $7.3x10^{-10}m^2.s^{-1}$. Assuming the viscosity of the solution to be that of water at 25°C, taking the mean mole-fraction to be

5.6×10^{-4} (equivalent to $3 g.l^{-1}$ furfural), and using an average bed-voidage of 0.7 at a superficial liquid velocity of $0.024\ m.s^{-1}$ - see section 5.5 - the mass transfer coefficient in a fluidised bed of CS-15 was estimated to be $0.06\ m.s^{-1}$.

The Biot number corresponding to this mass-transfer coefficient - see section 4.6.2 for the value of D_s^* - for the furfural/CS-15 system is:

$$\text{Biot} = \frac{K_L r_o}{D_s^*} = \frac{0.06\ m/s \times 0.82\times10^{-3}\ m}{4.28\times10^{-12}\ m^2/s}$$

$$= 5\times10^{6}$$

Similar calculations were performed for the remaining combinations of adsorbent and solute.

APPENDIX V - Physical and Fluidisation Properties of the Adsorbents

Properties such as particle densities, and voidages under different circumstances were measured as required. The measurements and theory required are summarised below.

V.1 - Determination of Particle Density

The experimental technique has been summarised in section 5.4. The equation used to calculate the particle density was derived as follows:

The volume of adsorbent in the measuring cylinder is:

$$V_s = (1-\epsilon)V_{bulk} \qquad \text{...(V/1)}$$

The value of ϵ for the adsorbent packed into the cylinder was measured as described in section 5.4, and eqn.(V/1) along with the definition of density gives the following result:

$$\rho_s = \frac{W_s}{V_s} = \frac{W_s}{(1-\epsilon)V_{bulk}} \qquad \text{...(V/2)}$$

Experimental measurements are summarised below:

Table V.1

Measurement of Adsorbent Density

		CS-10		CS-15
V_{bulk}	$[m^3]$ x10^3	0.250		0.250
Ws	[kg]	0.109		0.082
ϵ	[-]	0.434		0.360
			and hence	
ρ_s	$[kg.m^{-3}]$	773.0		510.0

V.2 Fluidised-bed Voidage Measurement

Since there is no cheap reliable method of measuring voidage in a fluidised-bed, this had to be done indirectly. The voidage may be estimated as follows:

Eqn.(V/2) may be solved for ϵ to give the following result:

$$\epsilon_b = 1 - \frac{W_s}{\rho_s V_b} = \frac{W_s}{\rho_s A_b h_b} \qquad \ldots(V/3)$$

Since W_s, ρ_s, and A_b are known, and the time-average value of h_b may be measured with acceptable accuracy, the voidage of the bed can be estimated using **eqn.(V/3)**.

Experimental measurements made to determine the voidage at different flowrates are summarised below.

Bed area was calculated from the bed diameter (9cm) to be $6.36 \times 10^{-3} m^2$.

Table V.2

Measurement of Bed-voidage at Various Liquid flowrates

CS-10 W_s=0.6 kg		CS-15 W_s=0.3 kg	
Q_l [l/s]	h_b [cm]	Q_l [l/s]	h_b [cm]
0.112	26.0	0.071	20.5
0.129	29.0	0.083	24.5
0.152	32.5	0.095	29.5
0.170	36.0	0.106	33.0
0.198	40.0	0.121	40.0
0.223*	43.5*	0.143	50.0
0.238	46.5		

* result is suspect

Application of eqn.(5/3) (with the bed-area calculated above and the particle densities from section V.1 above) gives the values of voidage from the bed-height recorded in Table V.2 above. It is standard practice to correlate such data using the 'superficial' velocity of the liquid, (which is defined as the velocity with which the liquid would flow if there were no adsorbent in the bed). The superficial velocity U_o is calculated by dividing the liquid flowrate by the bed-area.

The results in their final form of voidage at different superficial velocities are tabulated in section 5.4.3.

APPENDIX VI - Fluidised-bed Adsorbers

The equations describing fluidised-bed adsorbtion under simplifying assumptions are derived below. A boundary-layer theory solution to the simplified equations is developed, and experimental measurements of the unsteady-state adsorption in a fluidised bed are summarised.

VI.1 - Derivation of the governing equations

The following assumptions have been made to simplify the analysis - see section 7.2.1 for a discussion.

1) The adsorbent is perfectly mixed.
2) The liquid is in plug-flow.
3) The rate of adsorption can be characterised by an average concentration.

Under these assumptions, the model is simple enough to be derived by differential mass balances - see Muratov et al (1979) for the development of the full model (including nonideal mixing) via integral mass-balances.

The mass-balance is written as follows:

$$\underbrace{(Q_1 C)\Big|_z}_{\text{into } \Delta V} - \underbrace{r_a A_b a \, \Delta z}_{\text{adsorbed}} = \underbrace{(Q_1 C)\Big|_{z+\Delta z}}_{\text{out of } \Delta V} + \underbrace{\epsilon_b A_b \Delta x \frac{\partial C}{\partial t}}_{\text{accumulated}} \qquad \ldots(\mathrm{VI}/1)$$

Where r_a = rate of adsorption per unit adsorbent area [$\mathrm{kg.m^{-2}.s^{-1}}$]

a = surface area of adsorbent per unit bed-volume [$\mathrm{m^{-1}}$]

$= (1-\epsilon_b)\rho_s S_w$

S_w = surface area of adsorbent per unit mass [$\mathrm{m^2.kg^{-1}}$]

For dilute solutions, Q_1 is constant and is equal to U_oA_b. Making substitution, and dividing through by Δz, the desired result is achieved:

$$\frac{\partial C}{\partial z} = - \frac{r_a a}{U_o} - \frac{\epsilon_b}{U_o} \frac{\partial C}{\partial t} \qquad \ldots(VI/2)$$

$$= - \Psi - \frac{\epsilon_b}{U_o} \frac{\partial C}{\partial t}$$

Where $\Psi = \dfrac{r_a a}{U_o}$

VI.2 Development of a Boundary-layer Theory Solution

Boundary-layer theory assumes that propagation of disturbances in a system occurs at a finite velocity; these disturbances are confined to a certain (expanding) region of the system, the 'boundary-layer'.

The form of the solution within the boundary layer is assumed, one which gives the shape of solution expected. This functional form is substituted into the system equations and the analysis proceeds from there. The procedure employed for the simulation of unsteady-state adsorption in a fluidised bed is summarised below.

The following functional form for the time-dependent concnetration in the bed is assumed, since it has the expected shape:

$$\frac{C(z,t)}{C_{feed}} = \varphi(\eta) = 1 - 1.5\eta(z,t) + 0.5\left[\eta(z,t)\right]^3 \qquad \ldots(VI/3)$$

where $\eta(z,t) = \dfrac{z}{\delta(t)} \qquad 0 < \eta < 1$

The shape of the function φ is shown in Fig. VI.1. It is reasonable to expect a concentration profile of this shape, though one might expect instead a shape with zero derivative at

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$$= - \Psi - \frac{\epsilon_b}{U_o} \frac{\partial C}{\partial t}$$

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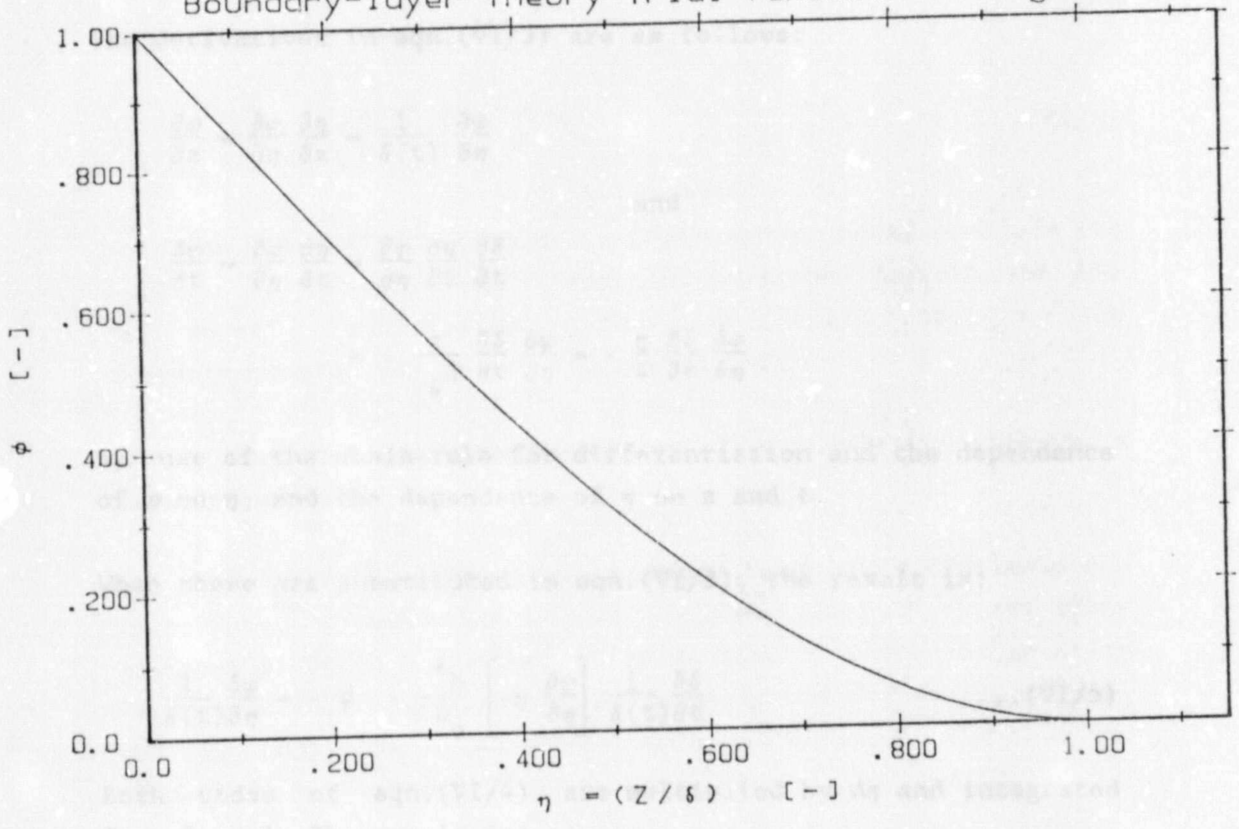
where $\eta(z,t) = \dfrac{z}{\delta(t)}$ $\qquad 0 < \eta < 1$

The shape of the function φ is shown in Fig. VI.1. It is reasonable to expect a concentration profile of this shape, though one might expect instead a shape with zero derivative at

Boundary-layer Theory Trial-function φ Fig. VI.1



$\eta=0$.

Substituting eqn.(VI/3) into eqn.(VI/2) the following result is obtained:

$$\frac{\partial\varphi}{\partial z} = -\psi - \frac{\epsilon_b}{U_o}\frac{\partial\varphi}{\partial t} \qquad \text{...(VI/4)}$$

Where $\psi = \Psi/C_{feed}$

The derivatives in eqn.(VI/3) are as follows:

$$\frac{\partial\varphi}{\partial z} = \frac{\partial\varphi}{\partial\eta}\frac{\partial\eta}{\partial z} = \frac{1}{\delta(t)}\frac{\partial\varphi}{\partial\eta}$$

and

$$\frac{\partial\varphi}{\partial t} = \frac{\partial\varphi}{\partial\eta}\frac{\partial\eta}{\partial t} = \frac{\partial\varphi}{\partial\eta}\frac{\partial\eta}{\partial\delta}\frac{\partial\delta}{\partial t}$$

$$= -\frac{z}{\delta^2}\frac{\partial\delta}{\partial t}\frac{\partial\varphi}{\partial\eta} = -\frac{\eta}{\delta}\frac{\partial\delta}{\partial t}\frac{\partial\varphi}{\partial\eta}$$

by use of the chain-rule for differentiation and the dependence of φ on η, and the dependence of η on z and t.

When these are substituted in eqn.(VI/3), the result is:

$$\frac{1}{\delta(t)}\frac{\partial\varphi}{\partial\eta} = -\psi - \frac{\epsilon_b}{U_o}\left[-\eta\frac{\partial\varphi}{\partial\eta}\right]\frac{1}{\delta(t)}\frac{\partial\delta}{\partial t} \qquad \text{...(VI/5)}$$

Both sides of eqn.(VI/4) are multiplied by $d\eta$ and integrated from 0 to 1. The result is:

$$\frac{M}{\delta(t)} = -\psi - \frac{\epsilon_b}{U_o}\frac{L}{\delta(t)}\frac{\partial\delta(t)}{\partial t} \qquad \text{...(VI/6)}$$

Where $M = \varphi(1) - \varphi(0) = 0 - 1 = -1$ and $L = \int_0^1 -\eta \frac{\partial \varphi}{\partial \eta} d\eta = \int_0^1 \varphi(\eta) d\eta$

For any choice of $\varphi(\eta)$ - see eqn.(VI/3) above - the constants M and L may be evaluated. Thus eqn.(VI/5) is a first-order, variables-separable ordinary differential equation in δ, with the initial condition $\delta(t=0) = 0$.

The solution to eqn.(VI/5) is:

$$\delta(t) = \frac{M}{\psi} \left[e^{-\psi U_o t/(\epsilon_b L)} - 1 \right] \qquad \ldots(\mathrm{VI}/7)$$

Thus at any time the boundary-layer theory model predicts the height to which the feed-concentration disturbance has penetrated (eqn.(VI/7)), and eqn.(VI/3) predicts the concentration at any point within that height.

(Note that the function ψ decreases with increasing time for a batch adsorber.)

In applying this model to the simulation of batch fluidised-bed operations, ψ must be evaluated - from the HSDM or any other acceptable model - for each point in time at which the solution is required. In this work, ψ was evaluated for various times, and an empirical exponential form was fitted to the rate vs. time data, see section VI.4

VI.3 - Experimental Results

The batch fluidised-bed adsorber was run for each combination of adsorbent and solute. The results and conditions are summarised in section 7.4.3, and are plotted in **Fig.'s 7.1 to 7.4**. There is nothing to add.

VI.4 Calculation of Rate of Adsorption for Boundary-layer Simulations

The rates of adsorption were calculated using the HSDM with the fitted mass-transfer parameters for each combination of adsorbent and solute, as described in section 7.4.1. Rates were calculated for concentrations equal to half the feed concentration and were correlated with an empirical exponential time expression of the form $r_a = fe^{gt}$, where t is exposure time in seconds. The average concentrations and the fitted parameters are summarised below.

Table VI.1

Average Concentrations

	CS-10 Runs $\hat{C}$ $[kg.m^{-3}]$	CS-15 Runs $\hat{C}$ $[kg.m^{-3}]$
Acetic Acid Runs	2.12	1.49
Furfural Runs	4.10	3.60

Table VI.2

Empirical Rate-equation Parameters

	CS-10		CS-15	
	f $[kg.m^{-2}.s^{-1}]$	g $[s^{-1}]$	f $[kg.m^{-2}.s^{-1}]$	g $[s^{-1}]$
Acetic Acid	1.13×10^{-4}	-0.015	1.59×10^{-4}	-0.039
Furfural	1.48×10^{-4}	-0.012	1.23×10^{-4}	-0.015

All of the correlation coefficients for linear log-log plots of rate vs. time were greater than 0.98, so these empirical fits are adequate for the purpose.

VI.5 Calculation of the Effective Rate of Adsorption, and the Effective Loading of the Exiting Adsorbent.

The analysis in both sections VI.5.1 and VI.5.2 is only valid if the **instantaneous rate of adsorption is a unique function of time.** In other words, any two particles exposed to the same concentrations for the same length of time have identical instantaneous rates of adsorption.

VI.5.1 Effective rate of adsorption

Since rate of adsorption varies with exposure time ('age'), and since there are particles of different ages in the steady-state fluidised-bed adsorber, the overall rate of adsorption must be calculated taking this into account.

The instantaneous rate of adsorption for a single particle depends on its age, t, and some effective concentrations $\underline{C}$:

$$r_{a,i} = r_{a,i}(\underline{C}, t)$$

The distribution of particle ages inside the adsorber is defined by the **internal age density function I(t)**. Thus, the fraction of particles in the adsorber with ages between t and t+dt is I(t)dt. The solid (adsorbent) phase is approximated as a being in a CSTR, for which the internal age density function is as follows (Levenspiel, 1962):

$$I(t) = \frac{e^{-t/\tau_s}}{\tau_s} \qquad \text{...(VI/8)}$$

The effective rate is a weighted integral of the rates of adsorption of the particles in the different age-classes, thus:

$$\hat{r}_{a,i}(\underset{\sim}{C},\tau_s) = \int_0^\infty I(t)\, r_{a,i}(\underset{\sim}{C},t)dt \qquad \text{...(VI/9)}$$

If the rate of adsorption is approximated by an exponential form as in VI.4, eqn.(VI/9) may be solved analytically to give:

$$\hat{r}_{a,i}(\underset{\sim}{C},\tau_s) = \frac{f_i(\underset{\sim}{C})}{1 + g_i(\underset{\sim}{C})\tau_s} \qquad \text{...(VI/10)}$$

See VI.7 for notation. Values of the f and g are not quoted, since they depend on the values of the concentrations.

VI.5.2 Effective loading of exiting adsorbent

Again, there is a distribution of ages among the exiting adsorbent. This distribution is described by the 'exit age density function E(t). Following the same arguments as in VI.5.1, the effective loading of the exiting adsorbent is given by:

$$\hat{\theta}_i(\underset{\sim}{C},\tau_s) = \int_0^\infty E(t)\ \theta(\underset{\sim}{C},t)dt \qquad \text{...(VI/11)}$$

The exit age density function Et) is as follows (Levenspiel, 1962):

$$E(t) = \frac{e^{-t/\tau_s}}{\tau_s}$$

Note that E(t) and I(t) are not generally the same, this is only the case for a perfect CSTR.

If the variation of the loading of a single particle with time is approximated by an (empirical) exponential function (which was found to adequately fit calculated data over a wide range of time and concentration) as follows,

$$\theta_i(\underset{\sim}{C},t) = \theta_{\infty,i}\left[1-e^{-f_i t}\right] \qquad \ldots(VI/12)$$

Where $\theta_{\infty,i}$ is the loading of component i in equilibrium with the concentrations $\underset{\sim}{C}$.

then eqn.(VI/12) may be solved analytically to give:

$$\hat{\theta}_i(\underset{\sim}{C},\tau_s) = \frac{\theta_{\infty,i} f_i \tau_s}{1 + f_i \tau_s} \qquad \ldots(VI/13)$$

Again, the f_i are functions of $\underset{\sim}{C}$ only.

VI.6 Estimation of the ratio of the effective rates.

The instantaneous rates of adsorption for simultaneous two component adsorption can be adequately correlated with an exponential form as follows:

$$r_{a,i} = f_i e^{g_i t} \qquad \ldots(VI/14)$$

Where the f and g are functions only of the liquid-phase concentrations $\underset{\sim}{C}$ to which the adsorbent is exposed.

The ratio of the instantaneous rates for a two-component system is as follows:

$$\frac{r_{a,1}}{r_{a,2}} = \frac{f_1}{f_2} \exp\left\{(g_1 - g_2\right\} \qquad \ldots(VI/15)$$

Since the ratio of the instantaneous rates declines slowly with time, as shown in Fig.7.5, it may be concluded that g_1 is fairly close to g_2. Now, from eqn.(VI/10), the ratio of the effective rates may be written as follows:

$$\frac{\hat{r}_{a,1}}{\hat{r}_{a,2}} = \frac{f_1}{f_2}\left(\frac{1 + g_2\tau}{1 + g_1\tau}\right) \qquad \ldots(VI/16)$$

and since the g are close, the above ratio may be approximated as f_1/f_2 for small values of τ Since the f are constants for a given set of liquid-phase concentration, the approximated ratio of the effective rates is also constant.

VI.7 Listing of FORTRAN 77 Program 'FSABS'

A computer program was written to carry out the steps of the design procedure as described in sections 7.5.5 and 7.5.6. A listing of the program follows.

```
C     Program 'FSABS'
C     Design of a continuous two-component fluidised-bed adsorber
C
      EXTERNAL ADSR, BNDYR, FADS, GCARB, MONTR, PDRT
      COMMON /PDISCR/ R(17), SCNC(2,17)
      COMMON /BOUND/ CBULK(2), IBTYP
      COMMON /PDAT/ PDENS, PDIAM
      COMMON /MTRANS/ BIOT, BETA(2), DSTAR(2)
      COMMON /DIMDAT/  CSTAR, RDIUS, QSTAR(2), A1(2), A2(2)
      COMMON /COMP/ ICMP, CNC(2)
      COMMON /DRV/ DERV(2)
      COMMON /ISFIT/ XKMN(2), XKMX(2), QSAT(2), XKPPA(2,2)
      COMMON /ADSRT/ RATEFT(2,2)
      COMMON /THFT/ THFIT(2,2), THNFN(2)
      COMMON /MINF/ CNCFD(2), CNCEF(2), AREAW, FLOWR
      REAL Y(2,17), THTLD(2,200), RATE(2,200), WKDO(700), DSURF(2),
     *   EXFTIM(200), CTEMP(2), CAVG(2), YREQ1(2),
     *   LQWRK(18), FTMAT1(3,3), FTMAT2(3,3), FRHS1(3), FRHS2(3),
     *   CARBRT(2), DYNTHT(2), THMBAL(2), DTHET(2), HBED(2),FDTHET(2),
     *   EXPTOP(1), THSM(2)
      DATA IFBDAT/1/, IDMRDT/2/, IPROFL/3/, ITERM/4/, ICOUT/6/,
     *   ICONC2/7/, IRATE/8/
C         Assign service data for root finding routine 'ZREAL2'
      TOL1=1.0E-3
      TOL2=TOL1
      SPRED=1.0E-1
      NSIG=3
      ITMAX=400
      NROOT=1
C         Set initial guess of adsorbent residence-time to 5 seconds
      EXPTOP(1)=5.0
C         CTYPE is the adsorbent type. This is used only as output.
      READ (IFBDAT,99) CTYPE
99    FORMAT (3X,A7)
C         Read in adsorption isotherm parameters
       READ (IFBDAT,*) QSAT(1), XKMN(1), XKMX(1)
       READ (IFBDAT,*) QSAT(2), XKMN(2), XKMX(2)
C         Read in physical characteristics of adsorbent.
       READ (IFBDAT,*) PDENS, PDIAM, AREAW
C         read in empirical fits of voidage vs. U0  e=avd.exp(bvd*U0)
       READ (IFBDAT,*) AVD, BVD
       READ (IFBDAT,*) BIOT
       READ (IFBDAT,*) BETA(1), DSTAR(1), BETA(2), DSTAR(2)
C         read in the loading of the feed-adsorbent
       READ (IFBDAT,*) FDTHET(1), FDTHET(2)
       READ (IFBDAT,*) U0
C         Calculate bed-voidage = a.U0**b
       VOID=AVD*(100.0*U0)**BVD
C      WRITE(ITERM,*)'VOIDAGE ',AVD, BVD,VOID,U0
       READ (IFBDAT,*) CSTAR
       RDIUS=PDIAM/2.0
       PI=3.1415926
C         Set flowrate and calculate bed area and diameter
      FLOWR=120.0/3600.0
      ABED=FLOWR/U0
      BDIAM=2.0*SQRT(ABED/PI)
C
C         Calculate the KAPPA matrix for 2 compt. adsorption isotherm
```

```
        DO 13 I=1,2
           DO 14 J=1,2
              T1=ALOG(XKMX(J)/XKMN(J))
              T2=ALOG(XKMX(I)/XKMN(I))
              XKPPA(I,J)=T1/T2
14         CONTINUE
13      CONTINUE
        ICMP=1
C           Calculate 'QSTAR' for each compt.
        CTEMP(1)=1.0
        QSTAR(1)=1.0
        CTEMP(2)=0.0
        QSTAR(2)=1.0
        CALL ISOTH (CTEMP, QSTAR)
        WRITE(ITERM,*)CTEMP(1), QSTAR(1)
        Q1=QSTAR(1)
        ICMP=2
        CTEMP(1)=0.0
        QSTAR(1)=1.0
        CTEMP(2)=1.0
        QSTAR(2)=1.0
        CALL ISOTH (CTEMP, QSTAR)
        WRITE(ITERM,*)CTEMP(2), QSTAR(2)
        QSTAR(1)=Q1
C         Cstar & Qstar are used to render the euqations dimensionless
C          'QSTAR' is the amount adsorbed in equil. with 'CSTAR'
        READ (IFBDAT,*) CNCFD(1), CNCEF(1), CNCFD(2), CNCEF(2)
        READ (IFBDAT,*) XMIN
C       Calculate 'A1','A2' & CAVG, terms used in boundary conditions
C       A1(1)=3.0*WCARB*QSTAR(1)/SVOL/CSTAR
C       A1(2)=3.0*WCARB*QSTAR(2)/SVOL/CSTAR
        A2(1)=CSTAR/PDENS/QSTAR(1)
        A2(2)=CSTAR/PDENS/QSTAR(2)
        CAVG(1)=(CNCFD(1)+CNCEF(1))/CSTAR/2.0
        CAVG(2)=(CNCFD(2)+CNCEF(2))/CSTAR/2.0
C
C
        CBULK(1)=CAVG(1)
        CBULK(2)=CAVG(2)
        RLRD0=3.0E-4
        ABRD0=0.0
        R0=0.0
        RMAX=1.0
        ABRI=0.0
        RLRI=0.001
        INORM=2
        IWKD0=700
        NPDE=2
        MSPC=2
        IBAND=NPDE
        IFAIL=0
C            Read in particle mesh and initial copnditions
        READ (IDMRDT,*) NRPTS
        DO 10 I=1,NRPTS
        READ (IDMRDT,*) Y(1,I), R(I)
        Y(1,I)=FDTHET(1)/QSTAR(1)
10      Y(2,I)=FDTHET(2)/QSTAR(2)
C            at t=0, particle surface is exposed to average bulk conc.
```

```
        DO 11 ICMP=1,2
           CALL ISOTH (CAVG, YREQ1)
           THNFN(ICMP)=YREQ1(ICMP)*QSTAR(ICMP)
            WRITE(ITERM,*)'THNFN = ',THNFN(ICMP), CAVG(ICMP)
11      Y(ICMP,NRPTS)=YREQ1(ICMP)
C           'THNFN' is the equilibrium loading for liquid conc.='CAVG'
        WRITE(ITERM,*)'Y|1= ',YREQ1(1),YREQ1(2)
        IND=0
        IPRT=1
        TIME=0.0
        READ (IDMRDT,*) NSTEPS, TSTEP, DUMY
C
C           IBTYP=0 -> DIRICHLET  |
C                                 |  BOUNDARY CONDITION TYPE
C           IBTYP=1 -> CAUCHY     |
C
        READ (IDMRDT,*) IBTYP, IPFREQ
C
        DO 20 ISTEP=1,NSTEPS
           TSTOP=TIME+TSTEP
           CALL D03PGE (NPDE, MSPC, PDRT, BNDYR,TIME, TSTOP, Y, NPDE,
     *                  NRPTS, R, RLRD0, ABRD0, INORM, MONTR, IPRT,
     *                  IBAND, WKD0, IWKD0, IND, IFAIL)
           TIME=TSTOP
C            Calculate flux of each component at adsorbent surface
           YREQ1(1)=Y(1,NRPTS)
           YREQ1(2)=Y(2,NRPTS)
           CALL DELTS(YREQ1, BETA, DSURF)
           DERV(1)=(Y(1,NRPTS)-Y(1,NRPTS-1))/(R(NRPTS)-R(NRPTS-1))
           DERV(1)=PDENS*DSTAR(1)*QSTAR(1)/RDIUS*DSURF(1)*DERV(1)
           DERV(2)=(Y(2,NRPTS)-Y(2,NRPTS-1))/(R(NRPTS)-R(NRPTS-1))
           DERV(2)=PDENS*DSTAR(2)*QSTAR(2)/RDIUS*DSURF(2)*DERV(2)
C          CALL ISOTH (CBULK, TH)
           IF (IFAIL.NE.0) THEN
              WRITE(ITERM,*)'IFAIL = ',IFAIL
              STOP
           END IF
           IFAIL=1
           IND=2
C
C                 Transfer local surface loadings to working matrix
C                 'SCNC'
           DO 30 I=1,NRPTS
              SCNC(1,I)=Y(1,I)
30         SCNC(2,I)=Y(2,I)
C
C                 Calculate loading 'THTLD' of each component.
C                 Store loadings, adsorption rates and exposure
C                 times for future use.
C
           EXPTIM(ISTEP)=TIME
           DO 31 ICMP=1,2
            RATE(ICMP,ISTEP)=DERV(ICMP)
              THTL=DCADRE (ADSR, R0, RMAX, ABRI, RLRI, ERR, IER)
31            THTLD(ICMP,ISTEP)=3.0*QSTAR(ICMP)*THTL
C     WRITE(IRATE,*)RATE(1,ISTEP)/RATE(2,ISTEP),
C    *               THTLD(1,ISTEP)/THTLD(2,ISTEP), TIME
      ISTP=ISTEP/IPFREQ
      XX=ALOG(1.0-THTLD(1,ISTEP)/THNFN(1))
```

```
      YY=ALOG(1.0-THTLD(2,ISTEP)/THNFN(2))
      IF((ISTP*IPFREQ).EQ.ISTEP) THEN
C         WRITE(IRATE,*)XX,YY,TIME
C         WRITE(IRATE,*)(RATE(1,ISTEP)), (RATE(2,ISTEP)), TIME
      END IF
20      CONTINUE
C
C                 Fit empirical forms to RATE vs EXPOSURE TIME, and
C                 LOADING vs EXPOSURE TIME
C                       RATE   =a.exp(b*t)
C                       LOADING=1-exp(d*t)
C                 Set parameters required by linear equation
C                 solution routine 'LEQT2F'
              IFTMAT=2
              NRHS=1
              IDGT=6
              IDIM=3
C
            DO 40 ICMP=1,2
              DO 41 I=1,3
                 DO 41 J=1,3
              FTMAT1(I,J)=0.000
41            FTMAT2(I,J)=0.000
C             FTMAT1(1,1)=NSTEPS
              FTMAT2(1,1)=NSTEPS
C
              THSM(1)=0.00
              THSM(2)=0.00
              TMSMQ=0.00
C                       Fit curve to loading vs exp. time values
              DO 42 IPNUM=1,NSTEPS
                 THSM(ICMP)=THSM(ICMP)+ALOG(1.0-THTLD(1,IPNUM)/THNFN
     *                          (ICMP))*EXPTIM(IPNUM)
                 TMSMQ=TMSMQ+EXPTIM(IPNUM)**2
C    *                          (ICMP))
C                FTMAT1(1,2)=FTMAT1(1,2)+ALOG(EXPTIM(IPNUM))
C                FTMAT1(2,2)=FTMAT1(2,2)+ALOG(EXPTIM(IPNUM))**2
C                FRHS1(1)=FRHS1(1)+ALOG(THTLD(ICMP, IPNUM))
C                FRHS1(2)=FRHS1(2)+ALOG(THTLD(ICMP, IPNUM))*
C    *                    ALOG(EXPTIM(IPNUM))
C                       Fit curve to rate vs exposure-time values
                FTMAT2(1,2)=FTMAT2(1,2)+EXPTIM(IPNUM)
                FTMAT2(2,2)=FTMAT2(2,2)+EXPTIM(IPNUM)**2
                FRHS2(1)=FRHS2(1)+ALOG(RATE(ICMP, IPNUM))
                FRHS2(2)=FRHS2(2)+ALOG(RATE(ICMP, IPNUM))*EXPTIM(IPNUM)
42            CONTINUE
              THFIT(1,ICMP)=-THSM(ICMP)/TMSMQ
              FTMAT2(2,1)=FTMAT2(1,2)
C          CALL LEQT2F(FTMAT1, NRHS, IFTMAT,IDIM,FRHS1,IDGT,LQWRK,IER)
C          THFIT(1,ICMP)=EXP(FRHS1(1))
C          THFIT(2,ICMP)=FRHS1(2)
           CALL LEQT2F(FTMAT2, NRHS, IFTMAT,IDIM,FRHS2,IDGT,LQWRK,IER)
           RATEFT(1,ICMP)=EXP(FRHS2(1))
           RATEFT(2,ICMP)=FRHS2(2)
           WRITE(IRATE,*)'THET',THFIT(1,ICMP),THFIT(2,ICMP), ICMP
40         WRITE(IRATE,*)'RATE',RATEFT(1,ICMP), RATEFT(2,ICMP), ICMP
           WRITE(ITERM,*)'RATE AND ADSCRPTION DATA ARE NOW FITTED'
C
C                 A column is now designed using the above rate and
C                 loading data.
```

```
C
C           Find the adsorbent residence time which produces the
C           required exit concentrations, and predicts
C           the same bed-height for each component.


          CALL ZREAL2(GCARB, TOL1, TOL2, SPRED, NSIG, NROOT, EXPTOP,
     *                ITMAX, IER)
          TAU=EXPTOP(1)
          WRITE(ITERM,*)'ROOT AT EXPOSURE TIME = ',TAU
C            Calculate  final bed parameters
            DO 62 ICMP=1,2
              CARBRT(ICMP)=(CNCFD(ICMP)-CNCEF(ICMP))/ADSRTE(TAU)/TAU
     *                         /AREAW*FLOWR
              DYNTHT(ICMP)=THTIME(TAU)
              THMBAL(ICMP)=FLOWR*(CNCFD(ICMP)-CNCEF(ICMP))
     *                         /CARBRT(ICMP)
              DTHET(ICMP)=(DYNTHT(ICMP)-FDTHET(ICMP))/THMBAL(ICMP)
              HBED(ICMP)=TAU*CARBRT(ICMP)/(1.-VOID)/PDENS/ABED
              WBED=TAU*CARBRT(1)
              IF (DTHET(ICMP).LE.0.0) HBED(ICMP)=99.99
62           CONTINUE
      WRITE(ITERM,*)CARBRT(1),CARBRT(2)
1001  FORMAT(' Activated carbon type                    : ',A7)
      WRITE(ICONC2,1001)CTYPE
      WRITE(ICONC2,*)'Average Particle Diameter     (mm)   :', PDIAM*1000.
      WRITE(ICONC2,*)'Acetic   (1) (feed,effluent) (g/l) :', CNCFD(1),
     *                                                         CNCEF(1)
      WRITE(ICONC2,*)'Furfural (2) (feed,effluent) (g/l) :', CNCFD(2),
     *                                                         CNCEF(2)
      WRITE(ICONC2,*)'Bed height                   (m)   :', HBED(1)
      WRITE(ICONC2,*)'Bed diameter                 (m)   :', BDIAM
      WRITE(ICONC2,*)'Carbon usage rate            (kg/s):', CARBRT(1)
      WRITE(ICONC2,*)'Total carbon in bed (kg)     (kg)  :', WBED
      WRITE(ICONC2,*)'Loading (feed solids) (1,2)  (-)   :', FDTHET(1),
     *                                                         FDTHET(2)
      WRITE(ICONC2,*)'Loading (exit.solids) (1,2)  (-)   :', DYNTHT(1),
     *                                                         DYNTHT(2)
      WRITE(ICONC2,*)'Ratio (dyn./massbal)         (-)   :', DTHET(1),
     *                                                         DTHET(2)
        STOP
        END
C
C           'PDRT' defines the particle diffusion equation
      SUBROUTINE PDRT (NPDE, RAD, TME, Y, DYDR, F,G,C)
      COMMON /MTRANS/ BIOT, BETA(2), DSTAR(2)
      COMMON /DIMDAT/  CSTAR, RDIUS, QSTAR(2), A1(2), A2(2)
      COMMON /DRV/ DERV(2)
      REAL C(NPDE), Y(NPDE), F(NPDE), G(NPDE,NPDE), DYDR(NPDE)
      REAL DSURF(2)
      IF (RAD.GE.0.99) THEN
        DERV(1)=DYDR(1)
        DERV(2)=DYDR(2)
      END IF
        C(1)=RDIUS**2/DSTAR(1)
        C(2)=RDIUS**2/DSTAR(2)
        CALL DELTS(Y, BETA, DSURF)
```

```
        G(1,1)=DSURF(1)
        G(1,2)=0.0000
        G(2,1)=0.0000
        G(2,2)=DSURF(2)
        F(1)=0.0
        F(2)=0.0
      RETURN
      END
C
C          'BNDYR' defines the particle diffusion boundary cond.'s
      SUBROUTINE BNDYR (NPDE, TIME, Y, IBND, P, Q, R)
      COMMON /BOUND/ CBULK(2), IBTYP
      COMMON /PDAT/ PDENS, PDIAM
      COMMON /MTRANS/ BIOT, BETA(2), DSTAR(2)
      COMMON /DIMDAT/  CSTAR, RDIUS, QSTAR(2), A1(2), A2(2)
      COMMON /COMP/ ICMP, CNC(2)
      REAL P(NPDE), Q(NPDE), R(NPDE), Y(NPDE), CSRF(2),THET(2), DSURF(2)
        P(1)=0.00E0
        Q(1)=1.00E0
        R(1)=0.00E0
        P(2)=0.00E0
        Q(2)=1.00E0
        R(2)=0.00E0
C
C         IF AT PARTICLE-LIQUID INTERFACE, EVALUATE BOUNDARY
C         CONDITION TERMS
        IF (IBND.EQ.1) THEN
C                THIS SECTION FOR DERIVATIVE B.C'S
          IF (IBTYP.EQ.1) THEN
C              CALCULATE THE SURFACE-DIFFUSION COEFFICIENT
               CALL DELTS (Y, BETA, DSURF)
C              CALCULATE FILM-CONCENTRATION FROM SURFACE LOADING
          DO 10 ICMP=1,2
C              CALL INVISO (Y, CSRF)
10           R(ICMP)=BIOT*A2(ICMP)/DSURF(ICMP)*(CBULK(ICMP)-CSRF(ICMP))
               RETURN
            END IF
C                THIS SECTION FOR DIRICHLET B.C
          IF (IBTYP.EQ.0) THEN
               P(1)=1.0
               Q(1)=0.0
               P(2)=1.0
               Q(2)=0.0
          DO 20 ICMP=1,2
               CALL ISOTH (CBULK, THET)
20           R(ICMP)=THET(ICMP)
               RETURN
            END IF
        END IF
          IF ((IBTYP.NE.0).AND.(IBTYP.NE.1)) THEN
          WRITE(4,*)'SPECIFY BOUNDARY CONDITION TYPE'
          STOP
          END IF
      RETURN
      END
C
C          'MONTR' monitors the solution of particle 'PDE' if desired
      SUBROUTINE MONTR (NPDE,R,NRPTS,TME,TLAST,Y,IY,TSTOP,TSTEP)
      COMMON /DIMDAT/  CSTAR, RDIUS, QSTAR(2), A1(2), A2(2)
```

```
      COMMON /DRV/ DERV(2)
      REAL Y(NPDE,NRPTS), R(NRPTS)
C         DO 10 J=8,NRPTS
C10         WRITE(3,*) Y(1,J)*QSTAR(1), Y(2,J)*QSTAR(2), R(J), TME
C       WRITE(3,*)
      RETURN
      END
C
C         'ADSR' interpolates the discrete adsorbance profile data
      REAL FUNCTION ADSR (RAD)
      REAL ADS(2)
      COMMON /PDISCR/ R(17), SCNC(2,17)
      COMMON /COMP/ ICMP, CNC(2)
        DO 10 I=1,17
10      IF (R(I).GT.RAD) GOTO 20
        IF (RAD.GT.R(17)) THEN
                WRITE(4,*)'ERROR IN PARTICLE INTERPOLATION'
                STOP
        END IF
20    ADS(ICMP)=(SCNC(ICMP,I)-SCNC(ICMP,I-1))/(R(I)-R(I-1))*(RAD-R(I-1))
        ADS(ICMP)=ADS(ICMP)+SCNC(ICMP,I-1)
        ADSR=ADS(ICMP)*RAD**2
      RETURN
      END
C
C
C          SUBROUTINE 'DELTS' RETURNS THE SURFACE DIFFUSION
C          COEFFICIENT AND ITS DERIVATIVE GIVEN SURFACE ADSORPTION
C
      SUBROUTINE DELTS (YADS, BETA, DS)
      REAL YADS(2), BETA(2), DS(2)
      DO 10 ICMP=1,2
        DS(ICMP)=1.0
        IF (ABS(BETA(ICMP)).GT.0.01) THEN
           DS(ICMP)= EXP(BETA(ICMP)*YADS(ICMP))
        END IF
10    CONTINUE
      RETURN
      END
C
C         'ISOTH' calculates the 2 component adsorption isotherm
      SUBROUTINE ISOTH (CONC, THET)
      EXTERNAL FADS
      COMMON /DIMDAT/  CSTAR, RDIUS, QSTAR(2), A1(2), A2(2)
      COMMON /ISFIT/ XKMN(2), XKMX(2), QSAT(2), XKPPA(2,2)
      COMMON /COMP/ ICMP, CNC(2)
      REAL CONC(2), THET(2)
      IF(ICMP.GT.2) THEN
          THET(ICMP)=9.9E5
          RETURN
      END IF
      AER=0.0
      RER=0.0001
      CNC(1)=CONC(1)*CSTAR
      CNC(2)=CONC(2)*CSTAR
      THT=DCADRE(FADS, XKMN(ICMP), XKMX(ICMP), AER, RER, ER, IER)
      THT=THT*QSAT(ICMP)*CNC(ICMP)/ALOG(XKMX(ICMP)/XKMN(ICMP))
      THET(ICMP)=THT/QSTAR(ICMP)
      RETURN
```

```
      END
C
C           Function FADS calculates the integrand in the
C           isotherm equation
      REAL FUNCTION FADS(XKVAL)
      COMMON /ISFIT/ XKMN(2), XKMX(2), QSAT(2), XKPPA(2,2)
      COMMON /COMP/ ICMP, CNC(2)
      FADS=0.000E0
      DO 10 J=1,2
10       FADS=FADS+(XKVAL/XKMX(ICMP))**XKPPA(ICMP,J)*XKMX(J)*CNC(J)
      FADS=1.0/(FADS+1.0)
      RETURN
      END
C
C           'ADSRTE' calculates adsorption rate at a given time
C           from fitted data
      REAL FUNCTION ADSRTE (RESTM)
      COMMON /COMP/ ICMP, CNC(2)
      COMMON /ADSRT/ RATEFT(2,2)
      ADSRTE=RATEFT(1,ICMP)*(1.0-RATEFT(2,ICMP)*RESTM)
      RETURN
      END
C
C           'THTIME' calculates overall adsorbance at a given time
C            from fitted data
      REAL FUNCTION THTIME (RESTM)
      COMMON /COMP/ ICMP, CNC(2)
      COMMON /THFT/ THFIT(2,2), THNFN(2)
      XP=THFIT(1,ICMP)*RESTM
      THTIME=XP/(1.0+XP)*THNFN(ICMP)

      RETURN
      END
C
C           'GCARB' calculates the difference in carbon feedrates
C           (calculated from the two desired effluent concentrations).
C           When this difference is zero, the carbon flowrate is
C           that which is required to produce the SPECIFIED effluent
C           concentrations.                         ---------
      REAL FUNCTION GCARB(X)
      COMMON /COMP/ ICMP, CNC(2)
      COMMON /ADSRT/ RATEFT(2,2)
      COMMON /MINF/ CNCFD(2), CNCEF(2), AREAW, FLOWR
      REAL X(1), CARBRT(2)
      TAU=X(1)
      DO 10 ICMP=1,2
           CARBRT(ICMP)=(CNCFD(ICMP)-CNCEF(ICMP))/ADSRTE(TAU)/TAU
     *                /AREAW*FLOWR
10    CONTINUE
      GCARB=CARBRT(1)-CARBRT(2)
      ICMP=1
      RETURN
      END
```

Author Anderson Paul
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