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The modelling and design of an activated carbon adsorber for the recovery of organic components from a cellulose-plant effluent

Anderson, Paul

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the following differential equation; the corresponding boundary condition is given by eqn.(7/17).

$$\frac{\partial C_{f,1}}{\partial C_{f,2}} = \frac{\hat{\Psi}_1}{\hat{\Psi}_2} = \frac{\hat{r}_{A,1}(\hat{C}_1, \hat{C}_2, \tau_s)}{\hat{r}_{A,2}(\hat{C}_1, \hat{C}_2, \tau_s)} = \hat{\Phi}\,(\hat{C}_1, \hat{C}_2, \tau_s) \qquad \ldots(7/16)$$

$$C_{f,1}\left[C_{f,2} = C_{feed,2}\right] = C_{feed,1} \qquad \ldots(7/17)$$

Where $\hat{C}_1 = (C_{feed,1} + C_{ex,1})/2$ $[kg.m^{-3}]$

similarly for $\hat{C}_2$

Note

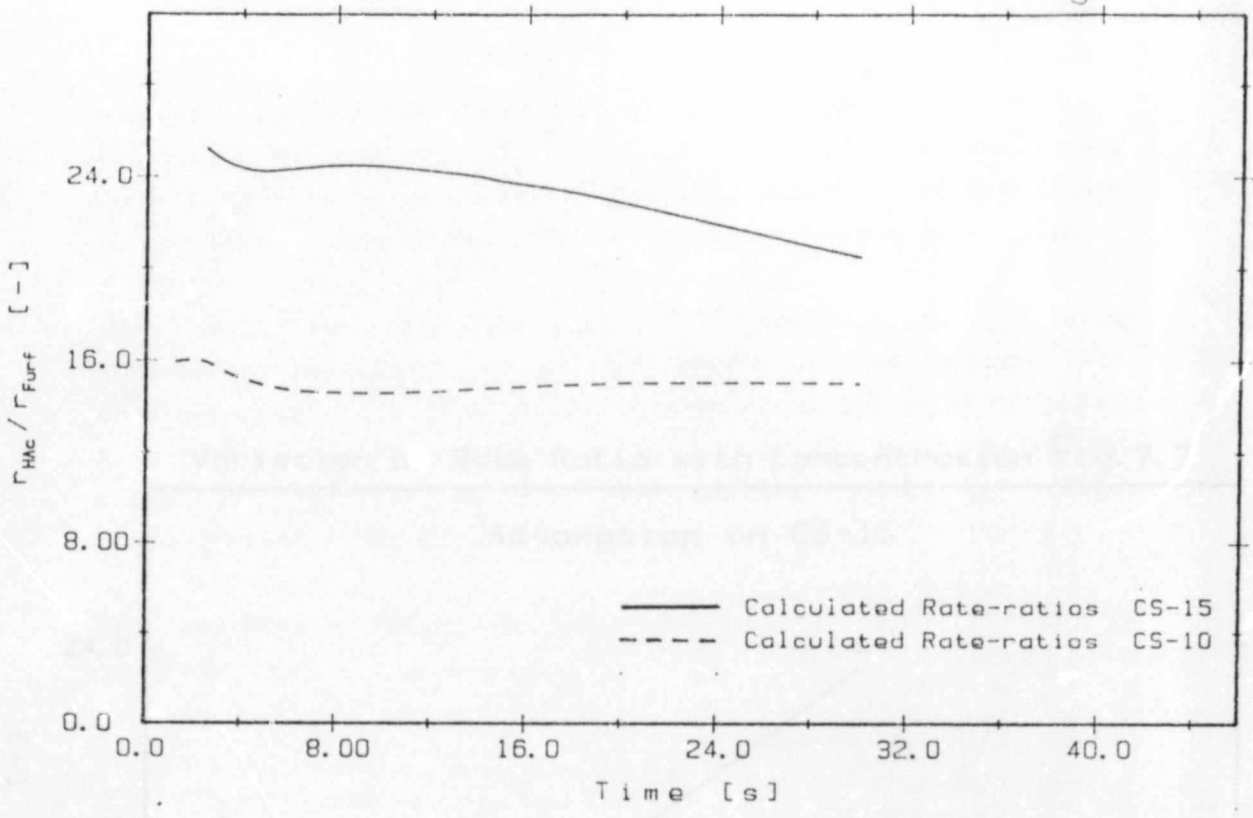
The solution to eqn.(7/16) consists of continuous set of pairs of concentrations. Choice of either of the two specifies the second one. Since the rate expressions are available - see sections 3.3.2 and 3.3.3 - eqn.(7/16) can be solved by the usual methods for ordinary differential equations.

7.5.4 A quick estimation of the effluent concentrations

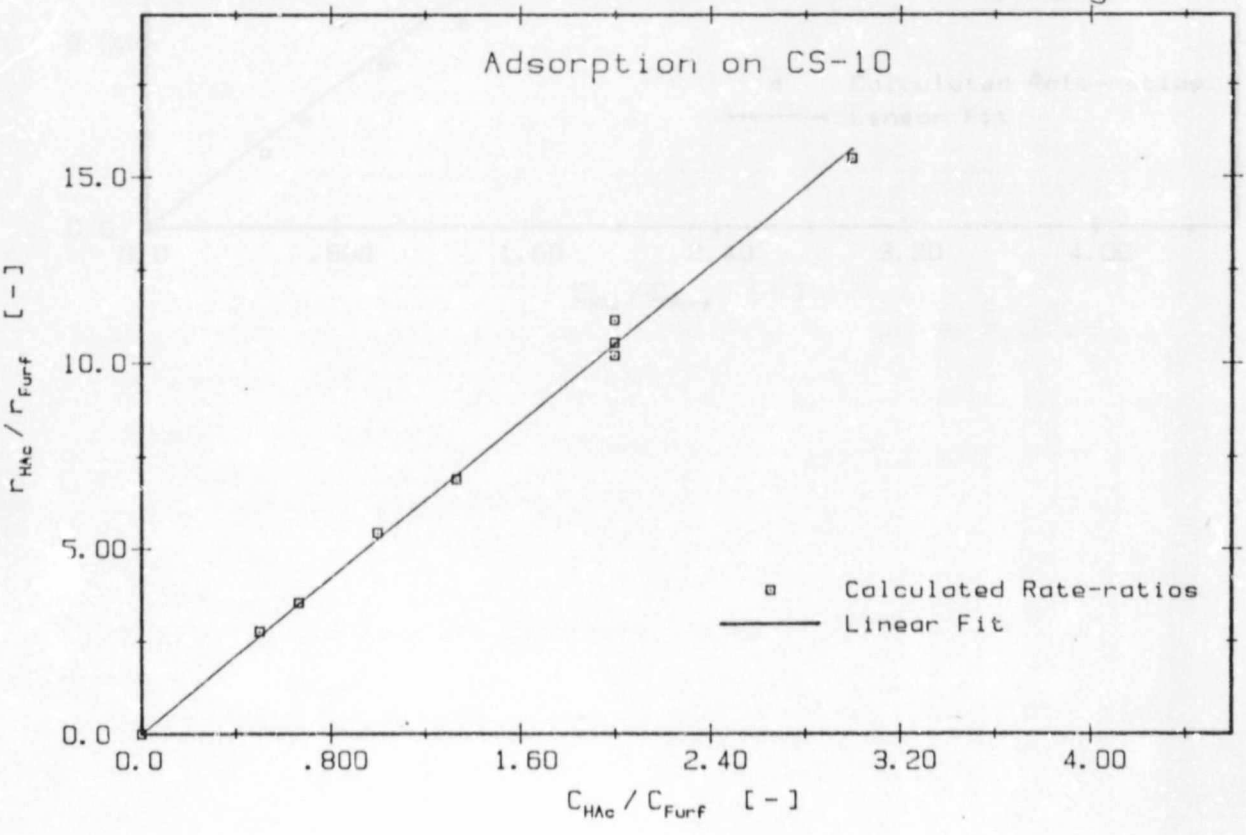
It is shown in APPENDIX VI that to a first approximation the ratio of the effective rates, $\hat{\Phi}$, can be considered equal to the ratio of the instantaneous rates, Φ, for low solid residence-times τ_s. Φ was evaluated numerically for various values of $\hat{C}_1$ and $\hat{C}_2$ over a range of times.

Φ was found to change slowly with time, as can be seen in the sample plots in Fig.7.5, so average values were considered. The ratio Φ, for given values of the average-concentration ratio $\hat{C}_1/\hat{C}_2$, was found to be largely independent of the particular values of $\hat{C}_1$ and $\hat{C}_2$. The variation of Φ with average-concentration ratio for each carbon type is shown in Figs.7.6 and 7.7 . The rate-ratio at an average concentration-ratio of 2 has been evaluated for three different

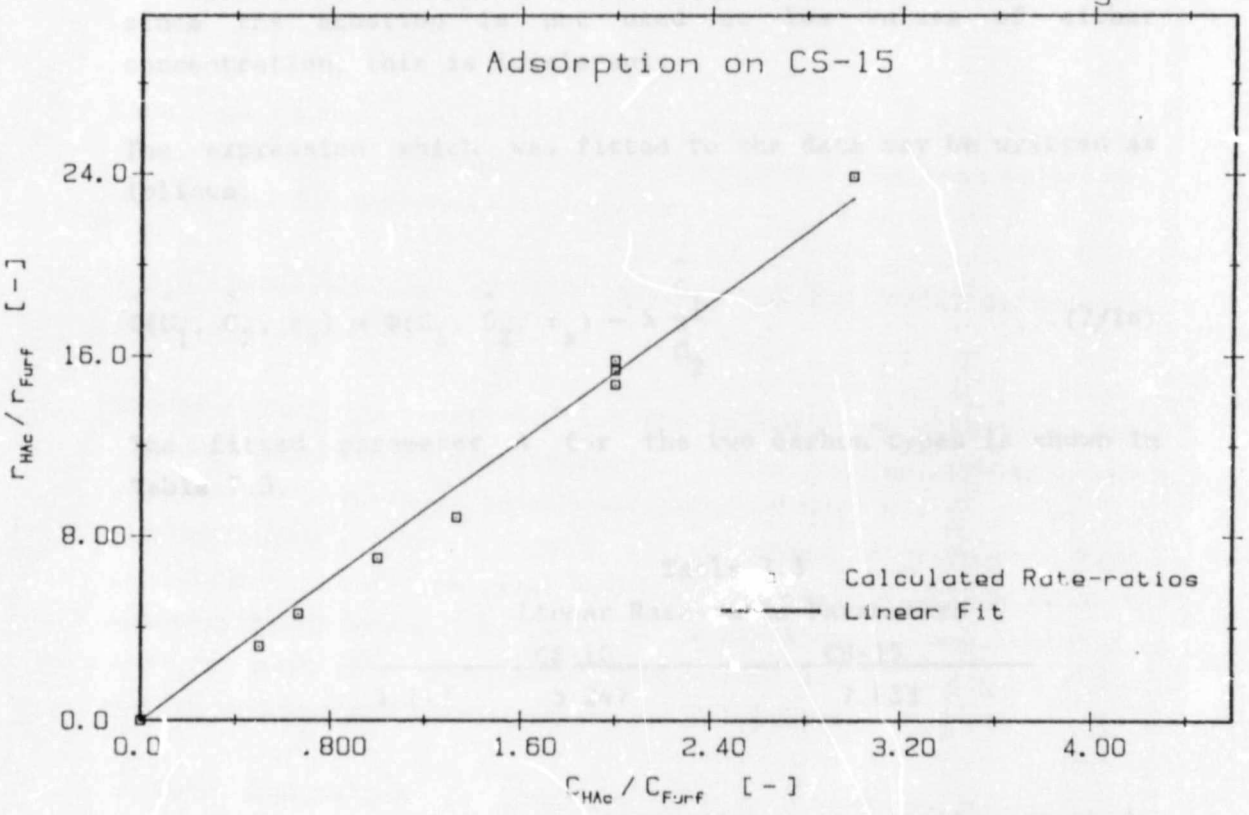
Variation of Rate-ratios with Time Fig. 7.5



Variation of Rate Ratio with Concentration Fig. 7.6



Variation of Rate Ratio with Concentration Fig. 7.7



sets of values of the individual average concentrations, namely: $\hat{C}_1$ = 2, 4, and 6 g/l; $\hat{C}_2$ = 1, 2, and 3 g/l. It can be seen that over this range of concentrations, which covers the liquor in question, there is very little variation in the rate-ratio.

The data in Figs.7.6 and 7.7 were correlated with zero-intercept linear forms, as shown on the graphs. The zero-intercept was selected for convenience. The rate-ratio for a vanishing average-concentration ratio need not be zero, but since the equation is not used at low values of either concentration, this is irrelevant.

The expression which was fitted to the data may be written as follows:

$$\hat{\Phi}(\hat{C}_1, \hat{C}_2, \tau_s) \approx \Phi(\hat{C}_1, \hat{C}_2, \tau_s) = \lambda \frac{\hat{C}_1}{\hat{C}_2} \qquad \ldots(7/18)$$

The fitted parameter λ for the two carbon types is shown in Table 7.3.

Table 7.3

Linear Rate-ratio Parameters

	CS-10	CS-15
λ [-]	5.247	7.633

Eqn.(7/16) as applied to exit conditions may now be written as follows:

$$\frac{\partial C_{ex,1}}{\partial C_{ex,2}} = \lambda \left(\frac{C_{feed,1} + C_{ex,1}}{C_{feed,2} + C_{ex,2}} \right) \qquad \ldots(7/19)$$

Boundary conditions are as before, in eqn.(7/17).

Eqn.(7/19) is separable and is easily solved; the solution is

merely quoted:

$$C_{ex,2} = \nu \left[\left(C_{ex,1} + C_{feed,1} \right)^{1/\lambda} \right] - C_{feed,2} \qquad \ldots(7/20)$$

where $\nu = \dfrac{2C_{feed,2}}{\left(2C_{feed,1}\right)^{1/\lambda}}$

Thus the exit concentration of component 1 can be calculated once the exit concentration of component 2 has been selected, and $\hat{\Psi}_1$ and $\hat{\Psi}_2$ can now be calculated.

7.5.5 Determination of the operational and design parameters for a specified duty

As discussed in section 7.5.2 the effluent concentrations may not be determined independently. Thus for the two-component system in question, the concentration of only one component in the effluent stream is chosen, and the other is calculated from eqn.(7/20). Once the inlet and effluent concentrations of both components are known, the rates of adsorption may be calculated, and in principle the adsorption column can be designed. The design problem may be summarised as follows:

- What **bed-height** is required to reduce both the acetic acid and furfural concentrations from their feed-concentrations to their effluent concentrations as calculated above ?
- What **bed-diameter** is required to ensure satisfactory operation of the adsorber ?
- What circulating mass flowrate of adsorbent is required to achieve this ?
- What make-up adsorbent flowrate is required to keep the adsorber effluent steady at the required concentrations ?

These questions are best answered mathematically. The design

equations are set out below, along with brief comments on each. The design procedure is summarised in point-form in section 7.5.6 .

Bed-height

The bed-height required for a certain duty is obtained by solving eqn.(7/15) for h_b:

$$h_b = \frac{C_{feed,1} - C_{ex,1}}{\hat{\Psi}_1} = \frac{C_{feed,2} - C_{ex,2}}{\hat{\Psi}_2} \quad \ldots(7/21)$$

Recall that the $\hat{\Psi}$ are both functions of both of the average-concentrations and the mean adsorbent residence-time (still to be determined). The above equality is necessary since the 'extents of adsorption' are dependent.

Bed-diameter

The bed-diameter, d_b, is specified by the volumetric-flowrate of the feed liquor, Q_1, and the superficial velocity, U_0, required to produce adequate fluidisation of the adsorbent being used. Thus:

$$A_b = \frac{Q_1}{U_o} \quad \text{and hence} \quad d_b = 2\left(\frac{A_b}{\pi}\right)^{\frac{1}{2}} \quad \ldots(7/22)$$

Circulating mass-flowrate of adsorbent

It shall now be shown that by selection of either the mass flowrate of adsorbent or the mean-residence time of the adsorbent, the design is completely specified.

Firstly, the mean residence-time, τ_s, of the adsorbent is defined as follows:

$$\tau_s = \frac{W_s}{G_s} \qquad \ldots(7/23)$$

Where W_s = mass of adsorbent in bed. See below [kg]
G_s = circulating mass-flowrate of adsorbent [$kg.s^{-1}$]

The bed-voidage ϵ_b depends on the superficial liquid-velocity which has already been selected above. The bed-height h_b is given by eqn.(7/21), in which the only outstanding parameter is the adsorbent mean-residence time which appears in the functions Ψ. Thus by choosing the mean-residence time, the volume of the expanded, fluidised bed, V_b, may be calculated:

$$V_b = A_b h_b \qquad \ldots(7/24)$$

And hence the mass of adsorbent in the bed may be calculated as follows:

$$W_s = V_b(1-\epsilon_b)\rho_s \qquad \ldots(7/25)$$

Now that the mean-residence time of the adsorbent has been selected, the circulating mass flowrate of the adsorbent can be calculated from a rearrangement of eqn.(7/23):

$$G_s = W_s/\tau_s \qquad \ldots(7/23')$$

Adsorbent make-up flowrate

The adsorbent make-up flowrate can be estimated as follows:

$$G_{s,m} = (1-\eta_r)G_s \qquad \ldots(7/26)$$

Where η_r is the fractional efficiency of regeneration - see section 2.6 for details and values. Since there are two different values for η_r, and hence two different make-up flowrates, the larger of the two flowrates calculated is used for operation.

Practical application of the design procedure is discussed below.

7.5.6 Practical design procedure

The procedure that was used to design a two-component fluidised-bed adsorber by the simplified method described above is summarised in point-form below.

1) Using the specified liquid-flowrate and the superficial liquid-velocity required for adequate fluidisation of the particular adsorbent, calculate the bed-diameter and bed-area. From the superficial liquid-velocity find the bed-voidage, see section 5.4.

2) Given the feed concentrations of each component, select the effluent concentration of one of them, and calculate the other from eqn.(7/20). Hence calculate the arithmetic-average concentrations of each component. Calculate the rates of adsorption and loadings for each component over a range of times t, using the two-component homogeneous surface-diffusion model with or without external mass-transfer resistance (see section 3.3.1 or 3.3.2 for details of the model). The values of θ^{o} in initial condition eqn.(3/8) are estimated from the regeneration efficiency data presented in section 2.5.

For convenience, fit (empirical) exponential forms to the rate of adsorption and loading values for each component (see APPENDIX VI for details).

3) For a selected adsorbent mean-residence time, and using the average concentrations from 2), calculate the rates of adsorption of each component onto the adsorbent in question using the empirical forms fitted in 2). Hence calculate $\hat{\Psi}_1$ and $\hat{\Psi}_2$ - see section 7.5.1.

4) Using the Ψ calculated in 3), and the feed- and effluent-concentrations from 2), calculate two bed-heights

using eqn.(7/21). In general, the bed-heights calculated from the two concentration differences will be different.

Repeat steps 1) to 4) until the adsorbent mean-residence time is found which gives equal bed-heights in eqn.(7/21). The residence time and bed-height thus found are the correct ones.

5) Using the bed-height obtained in 4), and the bed-area calculated in 1), calculate the bed-volume and mass of adsorbent in the bed from eqns. (7/24) and (7/25) respectively.

6) Using the mass of adsorbent in the bed from 5), and the mean residence-time from 4), calculate the circulating mass-flowrate of adsorbent from eqn.(7/23'). Calculate the adsorbent make-up rate from eqn.(7/26).

Before a design is accepted, the following checks must be made:

- Calculate the required increase in average specific-adsorbance for each component from a mass balance as follows:

$$\Delta\theta_{mb,i} = \frac{Q_l(C_{feed,i} - C_{ex,i})}{G_s} \qquad \ldots(7/27)$$

- Calculate the increase in the average specific adsorbance for each component using the segregated mixing model with the two-component adsorption model, as described in APPENDIX VI. This is the specific adsorbance that can be achieved by an average particle during its stay in the bed. Call this $\Delta\theta_{dyn,i}$, for dynamic limit.

Only designs in which both the $\Delta\theta_{dyn,i}$ are sufficiently greater than $\Delta\theta_{mb,i}$ are acceptable. The closest approach allowed between mass-balance and dynamic limits may be varied to suit the safety factor desired for each design. This check is reported as the adsorbance ratio, the ratio

$\Delta\theta_{dyn,i}/\Delta\theta_{mb}$.

Since the favorable effects of the completely fresh make-up adsorbent on the dynamic limit have been neglected, the safety factor in the design is larger than it appears to be. However, it is necessary to perform this test unless it can be proved that the dynamic limit is always larger than the mass-balance requirement.

A computer program was written to perform the various steps in the design procedure, from calculation of the adsorption rates from the two-component homogeneous surface-diffusion model for a range of exposure times, to finding the residence time required to give the desired performance, see 4). The program also performed the above calculations for checking the acceptability of the design; comparison of the $\Delta\theta$'s was done manually. A listing of the program may be found in APPENDIX VI.

7.6 Design Specifications for a Fluidised-bed Adsorber

An adsorber was designed for each of the two carbon types. The design specifications of each are summarised below. In both cases the specific adsorbance of the recycled adsorbent was estimated from the data presented in section 2.5 to be 10% of the expected maximum specific adsorbances of 0.05 and 0.1 for acetic acid and furfural respectively.

7.6.1 An adsorber using activated carbon type CS-10

Bed Dimensions			
	Bed Height	2.8	[m]
	d_b	1.3	[m]
Flowrate Specifications			
	Liquor Flowrate	120.0	[$m^3.hr^{-1}$]
	U_o	2.6	[$cm.s^{-1}$]
	Circulating Adsorbent Flowrate	17.0	[$kg.s^{-1}$]
	Adsorbent Make-up flowrate	3.0	[$kg.s^{-1}$]
Concentration Data			
	Feed Concentration - Acetic Acid	6.0	[$g.l^{-1}$]
	- Furfural	3.0	[$g.l^{-1}$]
	Exit Concentration - Acetic Acid	0.5	[$g.l^{-1}$]
	- Furfural	2.1	[$g.l^{-1}$]
Miscellaneous Information			
	Mass of Adsorbent in Bed	1 006.0	[kg]
	Adsorbance Ratio - Acetic Acid	2.5	[-]
	- Furfural	10.7	[-]
	Recovery rate - Acetic Acid	528.0	[$kg.hr^{-1}$]
	- Furfural	95.0	[$kg.hr^{-1}$]
	% Recovered from - Acetic Acid	73.0	[-]
	feed-stream - Furfural	26.0	[-]

7.6.2 An adsorber using activated carbon type CS-15.

Bed Dimensions			
Bed Height		1.7	[m]
Bed Diameter		1.33	[m]
Flowrate Specifications			
Liquor Flowrate		120.0	[$m^3.hr^{-1}$]
U_o		2.4	[$cm.s^{-1}$]
Circulating Adsorbent Flowrate		14.6	[$kg.s^{-1}$]
Adsorbent Make-up flowrate		1.5	[$kg.s^{-1}$]
Concentration Data			
Feed Concentration	- Acetic Acid	6.0	[$g.l^{-1}$]
	- Furfural	3.0	[$g.l^{-1}$]
Exit Concentration	- Acetic Acid	0.5	[$g.l^{-1}$]
	- Furfural	2.33	[$g.l^{-1}$]
Miscellaneous Information			
Mass of Adsorbent in Bed		160.0	[kg]
Adsorbance Ratio	- Acetic Acid	1.1	[-]
	- Furfural	9.1	[-]
Recovery rate	- Acetic Acid	462.0	[$kg.hr^{-1}$]
	- Furfural	74.8	[$kg.hr^{-1}$]
% Recovered from feed-stream	- Acetic Acid	64.0	[-]
	- Furfural	21.0	[-]

Special attention would have to be given to the design of a distributor for both of the above adsorbers, due to the large diameter to height ratios.

7.7 Conclusions

Although the experimental measurements on batch fluidised-bed adsorption are not conclusive, there is an indication that the calculated rates of adsorption are reasonable, since the model results are fairly close to experimental measurements.

As regards the physical process of fluidisation, the model may be improved by accounting for the varying concentration a particle 'sees' whilst travelling around the bed. One approach to this would be to model the fluidised solids as a series of slices (CSTR's) with intermixing between adjacent slices. By doing this, the effect of local adsorption rates could be included, thus substantially improving model reliability. The drawback of such an approach is that there are extra parameters, such as the degree of mixing between 'slices', which would be difficult to determine independently.

Further concluding remarks may be found in section 8.

8 Conclusions and Summary

The adsorption of furfural and acetic acid onto either CS-10 or CS-15 activated carbon in a fluidised-bed adsorber may be reasonably approximated as internal surface-diffusion controlled. The diffusion parameters D_s^* and β are easily estimated by matching model predictions to concentration histories in a batch stirred-tank adsorber, as discussed in section 4.

Once the mass-transfer parameters have been estimated, the design procedure is fairly simple to apply. However, there appears to be a conflict between the inter-dependence of the effluent concentrations, which forces a high concentration of furfural in the effluent, and the excessive magnitude of the furfural adsorbance ratio A large adsorbance ratio leads one to suppose that more furfural could possibly be removed from the liquid than specified above. The only way that could be done would be to violate the inter-dependence of the effluent concentrations. Thus these results have been accepted as estimates from a simplified design procedure.

It is clear from the rate-ratio parameter λ (see **Table** 7.3), and the design data presented in section 7.6 that acetic acid is far more quickly adsorbed on both adsorbents than is furfural, and that this effect is more pronounced for adsorption on CS-15. In view of this fact, the design of an adsorber to remove compounds with such disparate behaviour would be better if local rates, and not average-concentration based rates, were used. As mentioned in section 7.2 , this would entail statistical modelling of the fluidisation process, or substantial modification of the model with the introduction of extra parameters.

From a practical point of view, the large difference in rates can be used to advantage to achieve a degree of separation of solutes to a certain degree, as the designs above have predicted. It must be remembered, however, that the rates of

adsorption are calculated from a model that could be much improved by including the effects of pore-size distributions. It is strongly recommended that a more fundamental approach to fluidised-bed modelling be used for design work where an appreciable investment is at stake.

A decision as to which adsorbent type is optimum would only be possible after more extensive studies on recovery of adsorbates and regeneration of adsorbent have been done. It is recommended that the following be fully investigated:

1) The decomposition of furfural.

2) The regeneration of adsorbent, and the solute recovery process.

3) Continuous fluidised-bed adsorption of non-decomposing solutes, in order to validate the design procedure proposed here.

Full-scale adsorption units may then be optimally designed using this work, and the further work recommended above.

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APPENDIX I - Adsorption Isotherms and Adsorbent Regeneration

I.1 The Theory of Okazaki, Kage and Toei (1980)

A single component isotherm is proposed as follows:

1) Assume the surface of the adsorbent to be heterogeneous, i.e. it is made up of infinitesimal 'patches' with different adsorption energies.
2) Assume that the adsorption behaviour of each patch may be described by the Langmuir adsorption isotherm:

$$\frac{\theta}{\theta_{max}} = \frac{kC}{1 + kC} \qquad \ldots(I/1)$$

Where θ_{max} is the adsorbance at saturation.

3) Then the adsorption onto a finite amount of adsorbent is given by:

$$\frac{\theta}{\theta_{max}} = \int_{k_{min}}^{k_{max}} f(k) \frac{kC}{1 + kC} dk \qquad \ldots(I/2)$$

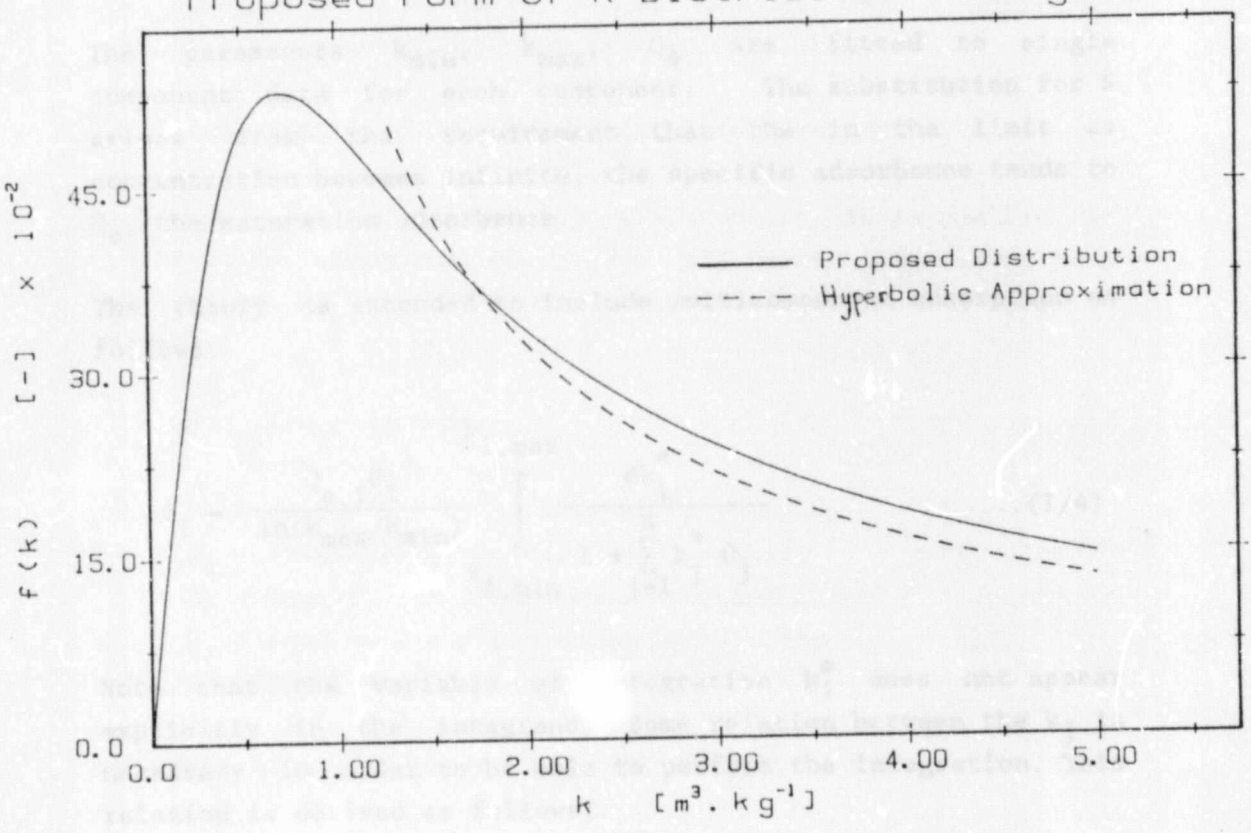
Where f(k)dk is the fraction of patches with adsorption energy between **k** and **k+dk**.

k_{min} and k_{max} are the values of the Langmuir parameter corresponding to the weakest and strongest 'patches' respectively.

Okazaki et al support a **k** distribution of the form shown in **Fig. I.1**, which they approximate as **f(k)=S/k**, where $k_{min}>0$, and **S** is a fitted parameter.

For a k distribution of this form, **eqn.(I/2)** can be

Proposed Form of k Distribution Fig. I.1



analytically integrated to give the following isotherm for single component adsorption:

$$\theta(C) = S \ln\left(\frac{1 + k_{max}C}{1 + k_{min}C}\right)$$

$$\theta(C) = \frac{Q_s}{\ln(k_{max}/k_{min})} - \ln\left(\frac{1 + k_{max}C}{1 + k_{min}C}\right) \qquad \ldots(I/3)$$

The parameters k_{min}, k_{max}, Q_s are fitted to single component data for each component. The substitution for S arises from the requirement that the in the limit as concentration becomes infinite, the specific adsorbance tends to Q_s, the saturation adsorbance.

The theory is extended to include multicomponent adsorption as follows:

$$\theta_i = \frac{Q_{s,i}C_i}{\ln(k_{max}/k_{min})} \int_{k_{i,min}}^{k_{i,max}} \frac{dk_i^*}{1 + \sum_{j=1}^{N} k_j^* C_j} \qquad \ldots(I/4)$$

Note that the variable of integration k_i^* does not appear explicitly in the integrand. Some relation between the k_j is necessary in order to be able to perform the integration. This relation is derived as follows:

4) Assume that interactions between molecules of adsorbate can be neglected irrespective of species.

5) Assume that the rank in the order of k among the 'patches' is independent of the species of adsorbate. The mathematics relating to this assumption is rather tedious and lengthy, and the reader is referred to the original publication for details.

The result of the above assumptions is:

$$k_j^* = \left(\frac{k_i^*}{k_{i,max}}\right)^{\kappa_{ij}} k_{j,max} \qquad \ldots(I/5)$$

Where $\kappa_{ij} = \dfrac{\ln(k_{j,max}/k_{j,min})}{\ln(k_{i,max}/k_{i,min})}$

The integration in eqn.(I/4) can now be done. Eqn.(I/4) constitutes the multicomponent adsorption isotherm.

I.2 Calculation of θ from Experimental Measurements

Isotherms are experimentally measured by determination of liquid-phase concentration before and after treatment with a known mass of adsorbent. A mass-balance on the solute is as follows:

$$V_l C_o = V_l C_\infty + W_s \theta \qquad \ldots(I/6)$$

Where V_l = volume of liquid treated by adsorbent [m^3]
C_o = initial liquid-phase concentration [$kg.m^{-3}$]
C_∞ = equilibrium liquid-phase concentration [$kg.m^{-3}$]
W_s = mass of adsorbent added to solution [kg]
θ = specific adsorbance [-]

Eqn.(I/6) is solved for θ to give:

$$\theta = \frac{V_l(C_o - C_\infty)}{W_s} \qquad \ldots(I/7)$$

I.3 Experimental Measurement of Adsorption Isotherms

The experimental measurements used to determine the isotherms are summarised in Tables I.1 and I.2 below:

Table I.1

Summary of Experimental Isotherm Measurements for CS-10

Acetic Acid

V_l [l]	W_s [g]	C_o [g/l]	C_∞ [g/l]	θ [-]
0.2	1.04	0.78	0.45	0.031
0.2	1.39	1.50	0.78	0.052
0.2	1.05	2.63	2.03	0.057
0.2	1.08	4.09	3.43	0.062
0.2	1.03	5.30	4.49	0.078
0.2	1.11	7.31	6.24	0.097
0.2	1.23	7.90	6.77	0.092

Furfural

V_l [l]	W_s [g]	C_o [g/l]	C_∞ [g/l]	θ [-]
0.2	2.12	0.38	0.02	0.034
0.2	2.00	0.38	0.05	0.033
0.2	2.10	0.81	0.18	0.060
0.2	2.10	0.81	0.19	0.057
0.2	2.05	1.97	0.89	0.105
0.2	2.20	1.97	1.00	0.088
0.2	2.06	3.32	1.80	0.148
0.2	2.02	3.32	1.88	0.143
0.2	2.04	4.44	2.90	0.150
0.2	2.05	7.23	5.19	0.199

Table I.2
Summary of Experimental Isotherm Measurements for CS-15

Acetic Acid

V_l [l]	W_s [g]	C_o [g/l]	C_∞ [g/l]	θ [-]
0.1	0.98	0.63	0.40	0.024
0.1	1.27	1.29	0.74	0.044
0.1	1.05	2.66	1.80	0.082
0.1	1.0	4.15	3.31	0.084
0.1	1.0	5.50	4.47	0.103
0.1	1.0	6.35	5.37	0.098
0.1	1.0	8.26	7.20	0.100

Furfural

V_l [l]	W_s [g]	C_o [g/l]	C_∞ [g/l]	θ [-]
0.2	3.11	1.06	0.17	0.058
0.2	4.16	1.14	0.29	0.041
0.2	4.06	2.33	0.69	0.081
0.2	4.01	3.42	1.15	0.113
0.2	3.07	3.35	1.31	0.133
0.2	4.07	4.48	1.77	0.133
0.2	4.13	5.43	2.23	0.155
0.2	3.17	5.45	2.79	0.168
0.2	3.95	6.81	3.02	0.192
0.2	4.07	8.11	3.53	0.220
0.2	3.19	7.88	3.99	0.244
0.2	3.17	10.17	5.32	0.306

The values of interest are C_{∞} and θ. These values are plotted in section 2.4 in Fig.'s 2.5 to 2.8.

I.4 Method of Fitting the Single-component Isotherm to the Experimental Data

The single component isotherm in eqn.(I/3) must be fitted to experimental data in order to apply the multicomponent adsorption isotherm in eqn.(I/4) above. The method used to do this was to minimise the sum of squares of errors between measured and predicted specific adsorption by choice of the three parameters Q_s, k_{min}, and k_{max}:

$$\underset{(Q_s,k_{min},k_{max})}{\text{Min}} \left[\theta(C_\infty) - \frac{V_1(C_o - C_\infty)}{W_s}\right]^2 \qquad \ldots(I/8)$$

Where $\theta(C_\infty)$ is given by eqn.(I/3).

This is a three-variable minimisation problem. Suitable minima were found for each measured isotherm using the IMSL routine 'ZXMIN', a quasi-Newton minimisation package. Fig.'s 2.5 to 2.8 show the predicted isotherms superimposed on the experimental data.

I.5 Regeneration of Adsorbent

The elementary studies on regeneration and re-use required only a few measurements to be made. These are summarised below. For both adsorbates the regeneration efficiency is defined by the new specific adsorbance as a percentage of the first specific adsorbance, and the percentage recovery is defined as the amount of solute in the wash solution (NaOH or benzene) as a percentage of that originally adsorbed.

I.5.1 Acetic acid related measurements

Since evaporation of adsorbed species would introduce errors into desorption efficiency measurements, special care had to be taken with these measurements. The procedure is summarised below.

1) A known mass of adsorbent was contacted with a solution of acetic acid. After sufficient time, the adsorbent was filtered out of the solution. The mass of acetic acid adsorbed was determined as described in section I.3 above.

2) The wet adsorbent was dried with a paper towel to remove as much of the wetting solution from the particles' exteriors as possible, since extended drying periods, or oven-drying tends to desorb the adsorbed species.

3) The adsorbent was immediately contacted with 0.1 N sodium hydroxide. After a sufficiently long time, the adsorbent was filtered out, and the concentration of acetate in the NaOH solution was measured by liquid-chromatography. Hence the amount of acetate removed from the adsorbent was determined, and so the percentage recovery from the adsorbent was calculated.

4) The adsorbent was then washed with water for a length of time equal to the time in 3) above, after which step 2) was repeated using the same volume of solution at the same concentration.
The results are summarised below.

Table I.3

Summary of Regeneration and Recovery Measurements

	First Adsorption				
	V_l [l]	W_s [g]	C_o [g/l]	C_∞ [g/l]	θ [-]
CS-10	0.1	1.0	5.83	4.43	0.116
CS-15	0.1	1.0	5.83	4.50	0.133

	Sodium Hydroxide Treatment				
	V_l [l]	W_s [g]	C_o [g/l]	C_∞ [g/l]	$V_l C_\infty$ [g]
CS-10	0.1	1.0	0.00	0.93	0.093
CS-15	0.1	1.0	0.00	0.93	0.093

	Second Adsorption				
	V_l [l]	W_s [g]	C_o [g/l]	C_∞ [g/l]	θ [-]
CS-10	0.1	1.0	5.83	4.88	0.095
CS-15	0.1	1.0	5.83	4.58	0.125

% recovery (CS-10) = 0.093/(0.583-0.443)*100 = 80%
% recovery (CS-15) = 0.093/(0.583-0.450)*100 = 70%
% regeneration (CS-10) = 0.095/0.116*100 = 82%
% regeneration (CS-15) = 0.125/0.133*100 = 94%

I.5.2 Furfural related measurements

Since decomposition and desorption of furfural would cause large errors in these measurements, special care was taken to take these measurements as quickly as possible. The procedure is described below.

1) A known mass of adsorbent was contacted with an aqueous solution of furfural. After sufficient contact time the

adsorbent was filtered out and the specific adsorption determined as before.

2) The adsorbent was again dried with a towel to remove any wetting solution that would give false recovery efficiencies. Oven drying in this case would hasten the decomposition of the adsorbed furfural.

3) The adsorbent was immediately added to a known volume of benzene, which had been pre-heated in a double-boiler heated by boiling water. Thus the temperature of the benzene was about 92°C. The boiling benzene-adsorbent mixture was stirred for approximately one hour. The neck of the flask was lightly sealed to prevent poisonous benzene fumes escaping, as well as to prevent loss of benzene and furfural. After about an hour, the adsorbent was filtered out of the hot benzene, towel dried, and placed into boiling water.

While the adsorbed benzene was being steam-stripped in the boiling water, the benzene solution was cooled and analysed for furfural concentration by UV transmittance spectroscopy. The amount of furfural removed from the adsorbent was calculated as before.

4) After the adsorbent had been boiled for sufficiently long, it was removed from the water, rinsed, dried and step 2) was repeated.
The results are summarised below.

Table I.4

Summary of Regeneration and Recovery Measurements

First Adsorption

	V_l [l]	W_s [g]	C_o [g/l]	C_∞ [g/l]	θ [-]
CS-10	0.1	2.08	3.38	0.16	0.155
CS-15	0.1	2.02	3.38	0.07	0.164

Benzene Treatment

	V_l [l]	W_s [g]	C_o [g/l]	C_∞ [g/l]	$V_l C_\infty$ [g]
CS-10	0.1	2.08	0.00	2.95	0.295
CS-15	0.1	2.02	0.00	3.06	0.306

Second Adsorption

	V_l [l]	W_s [g]	C_o [g/l]	C_∞ [g/l]	θ [-]
CS-10	0.1	2.08	3.20	0.42	0.134
CS-15	0.1	2.02	3.31	0.21	0.150

% recovery (CS-10) = 0.295/(0.338-0.016)*100 = 91%

% recovery (CS-15) = 0.306/(0.338-0.007)*100 = 92%

% regeneration (CS-10) = 0.134/0.155*100 = 86%

% regeneration (CS-15) = 0.150/0.164*100 = 92%

APPENDIX II - Theory of Diffusion

II.1 Analytical Solution to the HSDM model for Adsorption in an infinite bath.

The dimensionless equations describing adsorption from an infinite volume of well-stirred liquid may be written as follows:

$$\frac{\partial\theta}{\partial\tau} = \frac{1}{\xi^2}\frac{\partial}{\partial\xi}\left(\xi^2\frac{\partial\theta}{\partial\xi}\right) \qquad \ldots(II/1)$$

$$\theta(\xi,\tau{=}0) = \theta^{o}(\xi) = 0 \qquad 0 < \xi \leq 1 \qquad \ldots(II/2)$$

$$\theta(1,t) = \theta\left(\zeta_{bulk}\right) \qquad \tau \geq 0 \qquad \ldots(II/3)$$

$$\left.\frac{\partial\theta}{\partial\xi}\right|_{\xi=0} = 0 \qquad \tau \geq 0 \qquad \ldots(II/4)$$

Where the linearised dimensionless isotherm is given by $\theta{=}\zeta$. Now define ζ such that $\zeta_{bulk} = 1$ to simplify the solution.

Taking the Laplace transform of eqn.'s(II/1) to (II/4) with respect to time, the following equations result:

$$s\tilde{\theta}(\xi,s) = \frac{1}{\xi^2}\frac{\partial}{\partial\xi}\left(\xi^2\frac{\partial\theta}{\partial\xi}\right) \qquad \ldots(II/5)$$

$$\tilde{\theta}(\xi,s{=}0) = 0 \qquad 0 < \xi \leq 1 \qquad \ldots(II/6)$$

$$\tilde{\theta}(1,s) = \tilde{\theta}\left(\zeta_{bulk}\right) = \frac{\zeta_{bulk}}{s} = \frac{1}{s} \qquad \tau \geq 0 \qquad \ldots(II/7)$$

$$\left.\frac{\partial\tilde{\theta}(\xi,s)}{\partial\xi}\right|_{\xi=0} = 0 \qquad \tau \geq 0 \qquad \ldots(II/8)$$

The solution to eqn.(II/5) satisfying boundary condition

(II/8) is as follows:

$$\theta(\xi,s) = \frac{E}{\xi}\sinh(\sqrt{s}\xi) \qquad \ldots(II/9)$$

The arbitrary constant E is found by applying boundary condition (II/7) to eqn.(II/9). The result is as follows:

$$E = \frac{1}{s\,\sinh(\sqrt{s})}$$

and the final solution in the s domain is as follows:

$$\theta(\xi,s) = \frac{\sinh(\xi\sqrt{s})}{s\,\sinh(\sqrt{s})} \qquad \ldots(II/10)$$

The inverse transform of eqn.(II/10) can be found in tables. The solution is as follows:

$$\theta(\xi,\tau) = 1 + \frac{1}{\xi}\sum_{k=1}^{\infty}\frac{(-1)^k\, e^{-k^2\pi^2\tau}}{k\,\pi}\sin(k\pi\xi) \qquad \ldots(II/11)$$

If desired, the solution may be transformed back into dimensional form.

II.2 Application of a Mass-balance to find the Time-dependent Liquid-phase concentration in a finite-volume batch adsorber.

First, the average number of particles in a mass of adsorbent W_s is calculated as follows:

$$N_p = \frac{W_s}{\frac{4}{3}\pi r_o^3 \rho}$$

A mass-balance on the solute is written as follows:

$$VC(t=0) = VC(t) + N_p \int_0^{r_o} 4\pi r^2 \rho\theta(r,t)dr \qquad \ldots(II/12)$$

Where the integral on the right of eqn.(II/12) represents the amount of solute adsorbed onto one particle of adsorbent.

Substituting for N_p and simplifying, the following expression results:

$$C(t) = C(0) - \frac{3W_s}{V_1 r_o^3} \int_0^{r_o} r^2\theta(r,t)dr \qquad \ldots(II/13)$$

Eqn.(II/13) is the desired result, and may be transformed into dimensionless form as in eqn.(3/23).

II.3 Listing of FORTRAN 77 Program 'INTPART2'

A FORTRAN program was written to solve the system of two partial differential equations of the form (3/7). The method of solution and algorithm are discussed in section 6.2.

A listing of the program follows.

```
C     Program 'INTPART2'
C     Solution of the 2 component,nonlinear,unsteady-state
C     diffusion/adsorption equation (the HSDM equation)
      EXTERNAL ADSR, PDRT, BNDYR, MONTR, FADS
      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)
      REAL Y(2,17), WKD0(700), DSURF(2)
      REAL CTEMP(2), CONC0(2), C0(2), YREQ1(2)
      COMMON /ISFIT/ XKMN(2), XKMX(2), QSAT(2), XKPPA(2,2)
      DATA ISYS2D/1/, IRDAT/2/, IPROFL/3/, ITERM/4/, ICOUT/6/,
     *     ICONC2/7/, IRATE/11/
C     COMMON /HSPLIN/ H(15),YH(15),HSPLN(50,3),IHSPLN,NHPTS
C          Read in multicomponent adsorption isotherm data
        READ (ISYS2D,*) QSAT(1), QSAT(2)
        READ (ISYS2D,*) XKMN(1), XKMN(2)
        READ (ISYS2D,*) XKMX(1), XKMX(2)
C          Read in particle properties density, diameter, specific area
        READ (ISYS2D,*) PDENS, PDIAM, AREAW
        READ (ISYS2D,*) BIOT
        READ (ISYS2D,*) BETA(1), DSTAR(1), BETA(2), DSTAR(2)
        READ (ISYS2D,*) CSTAR
        RDIUS=PDIAM/2.0
C          Calculate the 'KAPPA' matrix (see Okazaki et al, 1980)
        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
        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 equations dimensionless
C         QSTAR is the adsorbance in equlibrium with CSTAR
        READ (ISYS2D,*) SVOL, CONC0(1), CONC0(2), WCARB
        READ (ISYS2D,*) XMIN
        WRITE(ICONC2,*)'BETA, C0, W ', BETA(1), BETA(2)
        WRITE(ICONC2,*)'            ', CONC0(1), CONC0(2), WCARB
C         Calculate 'A1','A2' & C0, terms used in the boundary condition
        A1(1)=3.0*WCARB*QSTAR(1)/SVOL/CSTAR
```

```
      A1(2)=3.0*WCARB*QSTAR(2)/SVOL/CSTAR
      A2(1)=CSTAR/PDENS/QSTAR(1)
      A2(2)=CSTAR/PDENS/QSTAR(2)
      C0(1)=CONC0(1)/CSTAR
      C0(2)=CONC0(2)/CSTAR
C
C
      CBULK(1)=C0(1)
      CBULK(2)=C0(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 conditions
      READ (IRDAT,*) NRPTS
      DO 10 I=1,NRPTS
      READ (IRDAT,*) Y(1,I), R(I)
10    Y(2,I)=Y(1,I)
C         at t=0, particle surface is at bulk-concentration
      DO 11 ICMP=1,2
        CALL ISOTH (C0, YREQ1)
     WRITE(ITERM,*)'ICMP = ',ICMP
11    Y(ICMP,NRPTS)=YREQ1(ICMP)
      WRITE(ITERM,*)'Y|1= ',YREQ1(1),YREQ1(2)
      IND=0
      IPRT=1
      TIME=0.0
      READ (IRDAT,*) NSTEPS, TSTEP, DUMY
C
C         IBTYP=0 -> Dirichlet  |
C                                | boundary condition type
C         IBTYP=1 -> Cauchy     |
C
      READ (IRDAT,*) IBTYP
C
      WRITE(ICONC2,*)C0(1)/C0(1), C0(2)/C0(2), TIME
      DO 20 ISTEP=1,NSTEPS
        TSTOP=TIME+TSTEP
C             Integrate the PDE's up to the new time value
        CALL D03PGE (NPDE, MSPC, PDRT, BNDYR,TIME, TSTOP, Y, NPDE,
     *               NRPTS,  R, RLRD0, ABRD0, INORM, MONTR, IPRT,
     *               IBAND, WKD0, IWKD0, IND, IFAIL)
        WRITE(ITERM,*)'SUCCESSFUL D03PGE CALL'
        TIME=TSTOP
        YREQ1(1)=Y(1,NRPTS)
        YREQ1(2)=Y(2,NRPTS)
        CALL DELTS(YREQ1, BETA, DSURF)
C
C             Calculate the gradients of each adsorbance at the
C             surface of the particle; hence calculate rate of adsn.
        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)
            WRITE(IRATE,*)(DERV(1)), (DERV(2)), TIME
            IF (IFAIL.NE.0) THEN
               WRITE(ITERM,*)'IFAIL = ',IFAIL
               STOP
            END IF
            IFAIL=1
            IND=2
            DO 30 I=1,NRPTS
               SCNC(1,I)=Y(1,I)
30          SCNC(2,I)=Y(2,I)
C            Calculate change in each of the liquid-phase concentrations
C            by finding the total mass of material adsorbed.
            DO 31 ICMP=1,2
              DELCON=DCADRE (ADSR, R0, RMAX, ABRI, RLRI, ERR, IER)
31            CBULK(ICMP)=C0(ICMP)-A1(ICMP)*DELCON
              WRITE(ICONC2,*) CBULK(1)*CSTAR/CONC0(1),
     *                        CBULK(2)*CSTAR/CONC0(2),TIME
20       CONTINUE
         STOP
         END
C
C     'PDRT' evaluates the coefficients of the terms in the PDE
C     (see section 6.2 for the form of equation solved by 'D03PGE')
C
      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)
C           Calculate each of the concentration-dependent surface
C           diffusion coefficients
        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' evaluates coefficients of the terms in the
C      boundary condition equations
C
      SUBROUTINE BNDYR (NPDE, TIME, Y, IBND, P, Q, R)
C           See section 6.2 for the form in which 'D03PGE' requires
C           the boundary conditions.
      COMMON /BOUND/ CBULK(2), IBTYP
      COMMON /PDAT/ PDENS, FDIAM
```

```
      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)
C
C           Default to the centre of the particle, i.e.
C           set P, Q & R to specify symmetry at the centre
        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 the
C           coefficients in the external boundary-condition
        IF (IBND.EQ.1) THEN
           IF (IBTYP.EQ.1) THEN
C                This section for Cauchy condition
C                If this section is actually to be used, the code
C                to evaluate the pore-fluid concentrations at the
C                particle surface 'CSRF(I)' must be inserted here
C
C              Calculate pore-fluid concentrations at particle
C              surface from the given adsorption values
C
C               <========== insert code here ==========>
C
           DO 10 ICMP=1,2
10         R(ICMP)=BIOT*A2(ICMP)/DSURF(ICMP)*(CBULK(ICMP)-CSRF(ICMP))
              RETURN
           END IF
C                This section for Dirichlet condition
           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
C           'MONTR' is used to monitor progress of the solution-
C           if required- without exiting from 'D03PGE'
      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
C 10      WRITE(3,*) Y(1,J)*QSTAR(1), Y(2,J)*QSTAR(2), R(J), TME
C        WRITE(3,*)
```

```
      RETURN
      END
C
C
C          'ADSR' interpolates the discrete values for adsorbance
C          to enable quadrature
      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(1)=(SCNC(1,I)-SCNC(1,I-1))/(R(I)-R(I-1))*(RAD-R(I-1))
        ADS(1)=ADS(1)+SCNC(1,I-1)
        ADS(2)=(SCNC(1,I)-SCNC(1,I-1))/(R(I)-R(I-1))*(RAD-R(I-1))
        ADS(2)=ADS(2)+SCNC(2,I-1)
        ADSR=ADS(ICMP)*RAD**2
      RETURN
      END
C
C          'INVISO' should 'invert' the multicomponent isotherm
C          and return the liquid-phase concentrations calculated
C
      SUBROUTINE INVISO (THET, CONC)
      COMMON /DIMDAT/  CSTAR, RDIUS, QSTAR(2), A1(2), A2(2)
      REAL THET(2), CONC(2)
C
C       <========= insert code here =========>
C
      RETURN
      END
C
C
C          'DELTS' returns the adsorbance-dependent surface-diffusion
C          coefficients given adsorbance of each components
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
C          'ISOTH' calculates the specific adsorbance of each
C          component given the liquid-phase concentrations
C
      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)
      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     'FADS' evaluates the denominator of the integrand
C     in the multicomponent adsorption isotherm of Okazaki et al (1980)
C
      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
```

APPENDIX III - Analytical Methods

III.1 Titrimetric Determination of Acetic Acid in SO_2 Solution

The titration is done in two steps, since direct titration for acetic acid is useless (dissolved SO_2 is acidic and would react with sodium hydroxide to give erroneous acetic acid concentrations).

The SO_2 is first titrated with iodine and thus converted to iodic acid and sulphuric acid:

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4 \qquad \ldots(III/1)$$

Notes

- The SO_2/acetic acid solution is titrated against an aliquot of standardised iodine, thus the amount of iodic and sulphuric acid produced is known.
- Acetic acid does not participate in the above reaction, so it is excluded from the equation.

The amount of H^+ formed in the above reaction is twice the number of moles of I_2. Thus for an iodine aliquot of 25 ml of 0.05 M I_2, the amount of H^+ formed is 0.005 moles.

The titrimetric determination of acetic acid then proceeds as usual. The now colorless solution composed of iodic, sulphuric and acetic acid, and water is titrated with 0.1M NaOH to the acetic acid endpoint of pH≈9, the phenolpthalein endpoint.

The amount of NaOH required to reach this endpoint is equal to the number of moles of H^+ formed in the first titration plus the number of moles of acetic acid in the solution:

Author Anderson Paul
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