Testing a Mathematical Model for Initial Chemical Reaction Fouling Using a Dilute Protein Solution

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ouling is defined as the accumulation of unwanted or undesirable, thermally insulating material on a heat transfer surface, resulting in a decrease in heat transfer efficiency and an increase in pressure drop.

A mathematical model for the initial chemical reaction fouling rate (Epstein, 1994) has successfully correlated the initial fouling rate data of Crittenden et al. (1987) for the solution polymerization of styrene, and has been further validated by Wilson and Watkinson (1996) for the autoxidation of indene in lube oil and by Vasak et al. (1995) for colloidal particle deposition under attractive double layer conditions. In addition, this model has been shown (Rose et al., 1997) to be qualitatively consistent with the experimental results achieved from a dilute whey protein solution.

According to the model, chemical reaction at, and attachment of the fouling deposit to, the heat transfer surface is treated as a rate process in series with mass transfer under turbulent flow conditions. As shown in the model development (Epstein, 1994), for a given fluid, chemical system and a fixed wall temperature, the chemical attachment coefficient (which bears the Arrhenius relationship to the wall temperature, and is proportional to the fluid residence time near the hot surface) is inversely proportional to the square of the friction velocity, and the mass transfer coefficient is directly proportional to this velocity. Therefore, at a given wall temperature it follows that, if the initial fouling rate is mass transfer controlled, e.g., at low fluid velocities, then as the velocity increases the deposition flux increases (Figure 1). If, however, the initial fouling rate is chemical attachment controlled, e.g., at high fluid velocities, then as the fluid velocity increases the deposition flux increases the deposition flux will decrease (Figure 1).

The model, written for turbulent flow in a duct, can be summarized mathematically, for a reaction of order n, by the equation:

$$C_{b} = \overline{k} \, \dot{R}_{fo} \, Sc^{\frac{2}{3}} \, V_{\bullet}^{-1} + \overline{k} \, \left(\dot{R}_{fo} \right)^{\frac{\gamma}{n}} \left(\frac{\rho e^{\frac{\Delta k}{p}} \overline{R}_{Tw}}{\eta} \right)^{\frac{\gamma}{n}} \, V_{\bullet}^{\frac{2}{n}} \tag{1}$$

in which the lefthand side represents the bulk concentration of the key component in the circulating solution, i.e., the overall driving force for fouling. The righthand side of this equation represents the product of initial fouling rate, R_{fo} , and mass transfer resistance in the first term, and of R_{fo} , and chemical attachment resistance in the second. Crucial to the second term is the time scaling factor, $\eta/\rho V_{\tau}^2$, associated with periodic shedding of the viscous sublayer or with fluid residence time at the wall.

A 1 wt% lysozyme solution was used as a model fluid to test a previously formulated mathematical model for the initial chemical reaction fouling rate of a heat transfer surface. The experimental results showed that, at a given wall temperature, a maximum initial fouling rate existed over a range of fluid velocities. The maximum rate and the fluid velocity at which it occurred both increased as the wall temperature increased. These observations were consistent with the model. Quantitatively, the average absolute percent deviation between the experimental results and the optimum model predictions was 23.3%. The decrease in initial fouling rate with increasing velocity at high fluid velocities was even greater than predicted by the model.

On a utilisé une solution de lysozyme de 1% en poids comme fluide modèle pour tester un modèle mathématique préalablement formulé pour la vitesse d'encrassement de réaction chimique initiale d'une surface de transfert de chaleur. Les résultats expérimentaux montrent qu'à une température de paroi donnée, il existe une vitesse d'encrassement initiale maximale dans une gamme de vitesses de fluide. La vitesse maximale et la vitesse de fluide auxquelles se produit l'encrassement augmentent toutes deux avec l'augmentation de la température. Ces observations concordent avec le modèle. Sur le plan quantitatif, l'écart en pourcentage absolu moyen entre les résultats expérimentaux et les prédictions du modèle optimales sont de 23,3%. La diminution de la vitesse d'encrassement initiale observée avec l'augmentation de la vitesse à de hautes vitesses de fluide est même plus importante que celle prédite par le modèle.

Keywords: fouling, chemical-reaction fouling, protein fouling, initial fouling rate, mathematical model.

It is this reciprocal square dependence of the initial fouling rate on fluid velocity that is the major innovation of the current model (Epstein, 1994).

With reference to Equation (1), the initial fouling rate \dot{R}_{fo} , the bulk concentration C_b and the friction velocity V. can be obtained from experimental data, while the purely kinetic activation energy ΔE , and reaction order *n*, can be obtained from the literature, or allowed to vary in the model. Once these and the

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Figure 1. The controlling limits of Equation (2).

fluid properties (p, η, Sc) are available, the above equation can be regressed to determine the best fit of the parameters \overline{k} and \overline{k} for all conditions of inside wall temperature (T_w) and fluid velocity (V). Hence, the true test of the model is whether single values of \overline{k} and \overline{k} (and ΔE and n) can correlate all the data over a wide range of V_* (including both a rise and a fall in \dot{R}_{fo} with V_*) and T_w .

If first order reaction kinetics can be assumed, then an equation explicit in R_{fo} , clearly showing the mass transfer and chemical attachment resistances, results from Equation (1):

$$\dot{R}_{fo} = \frac{C_b}{\frac{\bar{K} S c^{2/3}}{V_*} + \frac{\bar{\bar{K}} \rho e^{\Delta E / \bar{R} T_w} V_*^2}{\eta}}$$
(2)

The important features of the mathematical model are shown in Figure 2. Firstly, at a given wall temperature, there exists a maximum initial fouling rate over a range of fluid velocities; secondly, there is a clear wall temperature effect on the fouling rate including the maximum; and finally, the fluid velocity at which the maximum rate occurs increases as the wall temperature increases.



Figure 2. Features of the mathematical model.

To further the work performed using 1 wt% whey protein solutions at pH 6 (Rose et al., 1997), a pure protein extracted from chicken egg white, namely lysozyme, was chosen to serve as a model fluid to undergo denaturation and aggregation reactions leading to the deposition of insoluble material on the heat transfer surface (Visser and Jeurnink, 1997). Consistent with our previous work, a 1 wt% solution was used, but given that the isoelectric point of lysozyme is at approximately pH 11, the pH was adjusted to 8. The experiments were performed at low bulk temperatures (30°C to 52°C) and elevated clean, inside wall temperatures to study the fluid velocity and wall temperature effect of the aforementioned model in the absence of bulk reactions.

Experimental Setup

A schematic of the apparatus is shown in Figure 3 (Wilson, 1994). It consists of a flow loop in which the lysozyme solution is continuously recirculated from the holding tank through the heated test section ($d_i = 9.017$ mm), a series of double pipe coolers and back to the holding tank. The bulk inlet temperature was maintained at 30°C, while clean inside wall temperatures were varied from 52°C to 84°C. The test section itself is a 1.83 m long stainless steel tube with an outside diameter of 9.525 mm, a wall thickness of 0.254 mm and a heated length of 0.772 m, which is subjected to electrical resistance heating at a constant and uniform heat flux. Along the heated length are ten thermocouples which measure the local outside wall temperatures and an additional two measuring the inlet and outlet bulk fluid temperatures. The rise in temperature of each of these thermocouples gives a measure of the local fouling resistance at that temperature. Changes in bulk composition of the recirculating solution were found to be negligibly small during the course of a run (Rose, 1999).

Due to the longitudinal temperature gradient along the surface of the tube, it was the highest temperature thermocouples that exhibited the highest rates of fouling, and thus limited the duration of an experiment. Because clean inside wall temperatures were as high as 84°C, it was necessary to maintain some over-pressure on the test section to prevent the onset of boiling next to the wall as the wall temperature rose due to



Figure 3. Schematic of the Tube Fouling Unit (TFU).

fouling. When the test section pressure was maintained at 304 kPa, wall temperatures were allowed to rise to 120°C before terminating an experiment. Because of this temperature restriction, some data from the low temperature regions of the tube gave very low, and sometimes barely measurable initial fouling rates. For this reason, and to make data analysis easier, the criterion used by Paterson and Fryer (1988), where the induction period is defined as ending when the fouling deposit Biot number, $Bi = R_f U_o = (U_o/U) - 1 = 0.05$, was invoked. Thus, any data where the local heat transfer coefficient did not decrease by more than 5% of the clean heat transfer coefficient by the end of the experiment were neglected. Film Reynolds

numbers based on local fluid properties were varied from 2950 to 20715 to provide adequate data for a complete study on the velocity effect of initial fouling rates.

Batches of 1 wt% lysozyme solution were prepared in a 65 L mixing vessel, to ensure a well mixed solution without clumps or particulates. After mixing, the pH of the solution was adjusted to 8 with 0.1 N NaOH, and then added to the holding tank. The power to the test section was then applied to achieve the required operating conditions. Heating up the test section to steady state took approximately 15 min.

Experimental Results

Fouling in this system was primarily measured thermally, although mass deposition and pressure drop measurements could also be used. The local heat transfer coefficient at a given thermocouple location along the length of the test section was determined from the following equation, where Q was evaluated from the voltage and current applied to the test section, T_b from the bulk inlet and outlet fluid temperatures and T_w from the measured thermocouple temperature:

$$U = \dot{Q} / A(T_w - T_b) \tag{3}$$

The fouling resistance R_f was determined from:

$$R_f = 1/U - 1/U_o \quad (= x_f/\lambda_f = m_f/\rho_f \lambda_f) \tag{4}$$

and the initial fouling rate from:

$$\dot{R}_{fo} = dR_f / dt \Big|_{t=0} = d(1/U) / dt \Big|_{t=0}$$
 (5)

assuming that the solid-liquid heat transfer coefficient did not change with respect to time due to surface roughness effects or reduction in flow area. Depending upon the required Reynolds number, the flow rate and hence velocity of the fluid through the TFU was measured using one of three calibrated rotameters. The reported mass velocity is the time averaged value over the duration of the experiment.

Figure 4 shows a plot of the inside wall temperatures for the four highest temperature wall thermocouples from one experiment, which indicate a strong temperature effect on the initial fouling rate. All thermocouples in Figure 4 show a linear



Figure 4. Inside wall temperature profiles for TFU run 304 ($G = 523 \text{ kg/m}^2 \text{ s}$).



Figure 5. Reciprocal heat transfer coefficient at z = 713 mm for TFU run 304 ($G = 523 \text{ kg/m}^2 \text{ s}$). Open points are

increase in wall temperature with time after a brief delay or induction period (t_{d}) . This makes the analysis for initial fouling rate straightforward. In the region where the temperature is first increasing at a constant rate, the corresponding plot of reciprocal heat transfer coefficient versus time is linearly regressed and the slope is equal to the initial fouling rate, as shown in Figure 5.

Figure 6 shows an Arrhenius type plot for a given experiment, where ten individual thermocouple results were utilized to determine the wall temperature effect at a mass flux of 523 kg/m² s. The fouling activation energy was determined as 83.3 kJ/mol from a nonlinear least squares regression of $\ln R_{fo} = \ln A - \Delta E_f / \tilde{R}(T_{w,i})_c$. The results for all runs are presented in Table 1, showing a range in fouling activation energies from 29 to 118 kJ/mol, with an increase in fouling activation energy with increasing mass flux.

The increase of ΔE_f with mass flux (or fluid velocity) is consistent with the mathematical model. Using Equation (2) where n = 1, and assuming constant fluid physical properties and fully rough flow (f = constant), the model in its simplest form becomes:

$$\dot{R}_{f_0} = \frac{C_b}{\frac{1}{aV} + \frac{V^2}{\frac{-\Delta E_f}{he^{-\Delta E_f}\bar{R}_{T_{w,i}}}}} = Ae^{-\frac{\Delta E_f}{\bar{R}_{T_{w,i}}}}$$
(6)

For small fluid velocities, i.e., when mass transfer controls,

$$\dot{R}_{fo} = aVC_b = Ae^{-\Delta E_f / \bar{R}T_{w,i}}$$
(7)

indicating that the fouling activation energy approaches zero (fluid physical property variations with temperature would yield a non-zero but relatively small value of ΔE_i). For high fluid velocities, i.e., when chemical attachment controls,

$$\dot{R}_{fo} = \frac{be^{-\Delta E/\tilde{R}T_{w,i}}}{V^2} C_b = Ae^{-\Delta E/\tilde{R}T_{w,i}}$$
(8)

which, in turn, shows that the fouling activation energy approaches the purely kinetic activation energy. Therefore, by consideration of the mathematical model in the limits of the fluid velocity, it is expected that the observed fouling activation energy will increase with fluid velocity and approach the purely kinetic activation energy.

For this series of experiments it was determined that if an Arrhenius type expression were attached to the mass transfer term in Equation (2), i.e., allowing for the temperature dependence of diffusion, a diffusional activation energy of approximately 14 kJ/mol would be obtained. This value is significantly smaller than the

TFU Run	G (kg/m².s)	<i>Т_ь</i> (°С)	<u> (</u> kW)	ΔE _f (kj/mol)	In (A)	(T _{w,i}) _c (°C)
309	199.5	31-42	0.67	29.35	-1.56	59-84
306	296.9	31-50	1.71	45.76	5.03	64-82
310	297.2	31-50	1.71	49.01	6.08	63-81
307	412.3	31-50	2.35	84.85	18.59	6380
304	523.0	31-49	2.80	83.25	18.08	64 79
301	700.5	30-51	4.06	86.13	19.16	65–80
303	878.7	31-49	4.42	93.77	21.79	6679
308	991.3	31-49	4.96	115.24	28.22	68–79
305	1101.2	31-49	5.45	118.17	29.17	68–77

resulting purely kinetic activation energy of 155 kJ/mol, obtained assuming n = 1. These two activation energies bracket, and are therefore consistent with, the experimental fouling activation energies. From Table 1 it is possible to use the Arrhenius type expression to determine \dot{R}_{fo} at a given value of $T_{w,i}$ for each experiment and hence investigate the effect of mass velocity on initial fouling rate. Thus, Figure 7 shows three sets of results at wall temperatures where the initial fouling rate is strongly dependent upon the mass flux. In all cases one notes the presence of a maximum deposition rate at a critical mass flux as predicted by the model. Also, as the wall temperature decreases the value of the maximum \dot{R}_{in} decreases, and the location of the maximum shifts towards a decreasing mass flux, both trends again being consistent with the model. The three plots indicate a strong dependence of fouling rate on wall temperature, with appreciable differences in rates observed for only a 5°C temperature change.

Optimum Model Prediction

The experimental results from the fouling experiments were used to evaluate best fit values of the constants \overline{k} , \overline{k} , ΔE and n in Equation (1). Solution of this equation for N sets of data and j variables (\overline{k} , \overline{k} , ΔE , n) was achieved using a nonlinear least squares regression, by minimizing σ^2 in:

$$\sigma^{2} = \frac{\sum_{i=1}^{N} \left(\left[\dot{R}_{fo}(\text{expt}) - \dot{R}_{fo}(\text{model}) \right]^{2} \right)}{(N-j)}$$
(9)

The Levenberg-Marquardt method (Press et al., 1986), as previously employed by Vasak and Epstein (1996), uses a combination of Newton's method and a steepest-descent method to perform nonlinear curve-fitting to the experimental data. This procedure was employed here using FORTRAN 77.

The optimum modelling result ($\sigma^2 = 0.1785.10^{-10} (m^2 \cdot K/k)^2$) was achieved when the film temperature was used to evaluate the physical properties associated with the mass transfer term, and the wall temperature was used to evaluate the physical properties associated with the chemical attachment term. The optimum kinetic reaction order and activation energy were determined to be 0.75 and 161 kJ/mol, respectively. This compares reasonably well with 0.5 to 2 and 50 to 151 kJ/mol, respectively, reported in the batch kinetic studies of Makki (1996) as bracketing values of *n* and ΔE which vary unsystematically with pH. The average absolute percent deviation between the optimum model solution and the experimental



Figure 7(a). Effect of mass flux on initial fouling rate for 1% lysozyme solution at $(T_w)_c = 70^{\circ}$ C, $T_b = 30-52^{\circ}$ C.



Figure 7(b). Effect of mass flux on initial fouling rate for 1% lysozyme solution at $(T_w)_c = 75^{\circ}$ C, $T_b = 30-52^{\circ}$ C.



Figure 7(c). Effect of mass flux on initial fouling rate for 1% lysozyme solution at $(T_{w,i})_c = 80^{\circ}$ C, $T_b = 30-52^{\circ}$ C.

results was 23.3%. These results are illustrated in a parity plot in Figure 8.

Figure 9 shows a comparison of optimum model predictions with experimental data. The experimental results and model predictions display similar trends, previously discussed. In addition, Figure 9 shows that the bulk temperature, through its effect on the film temperature and hence the physical properties, has a significant effect on the model predictions, especially in the mass transfer controlled region. However, note that the decrease in experimental initial fouling rate in the chemical attachment dominated region is greater than that predicted by the model, suggesting an even greater inverse dependence on velocity. A similar result was obtained for some of the particulate fouling data reported earlier (Vasak et al., 1995). Since no existing models predict a greater than inverse second power dependence on fluid velocity, this is a problem for further enquiry.

Conclusions

The use of dilute lysozyme solutions has permitted a systematic study of the effect of mass velocity on the initial fouling rate. By maintaining low bulk temperatures to eliminate bulk reactions, the following experimental observations were made: a maximum initial fouling rate exists for a given wall temperature over a range of fluid velocities, and this maximum rate and the velocity at which it occurs both increase with increasing wall temperature. All of these observations, as with the earlier whey protein results (Rose et al., 1997), are qualitatively in agreement with the mathematical model.



Figure 8. Optimum model prediction for lysozyme solution fouling.



Figure 9. Comparison of model predictions to experimental data obtained by interpolation from the Arrhenius type equations. Dashed and solid lines, respectively, represent model based on lowest (inlet) and highest (exit) bulk temperature encountered in heated section.

Application of the model to the experimental fouling data yielded an optimum model solution with parameters (n, ΔE) which are consistent with the kinetic data presented by Makki (1996).

The fouling activation energy (ΔE_i) was shown to increase with mass flux, from a small diffusional value, to approach but never equal the purely kinetic activation energy (ΔE). This observation was consistent with the mathematical model (Epstein, 1994).

Although there was general agreement between experimental results and model predictions, the decrease in experimental initial fouling rate in the chemical attachment dominated region was even greater than the inverse second power dependence on velocity predicted by the model.

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Nomenclature

- a, b constants defined in Equation (6)
- pre-exponential constant in Arrhenius type expression, (m²·K/k]) Α A heat transfer surface area, (m²)
- Bi fouling deposit Biot number = $R_f U_o = (U^{-1} - U_o^{-1})U_o$
- Ć, bulk concentration of key component, (kg/m³)
- d inside tube diameter, (m)
- Ď diffusivity, (m²/s)
- ΔE chemical-kinetic activation energy, (kJ/mol)
- fouling activation energy, (kJ/mol) ΔE,
- f Fanning friction factor
- G fluid mass flux or mass velocity, (kg/m².s)
- number of unknown variables j
- k mass transfer constant in Equation (1), (kg²/s³·m²·K)
- Ī chemical attachment constant in Equation (1), $(kg^{n+1}/m^{3n}Ks)^{1/n}$
- level alarm low LAL
- deposit coverage of heat transfer surface, (kg/m²) m,
- order of surface reaction n
- number of experimental data points N
- PRV pressure relief valve
- **PSW** pressure switch
- Q power applied to test section, (kW)
- Ñ universal gas constant = $8.3143 \cdot 10^{-3}$, (k]/mol·K)
- R, fouling resistance, (m²·K/kW)
- Ŕ_{fo} initial fouling rate, (m² K/kJ)
- Schmidt number = $\eta/\rho D$ Sc
- t time, (s)
- t_d T delay period, (s)
- temperature, (K)
- TFU tube fouling unit
- ΤI temperature indicator
- U local overall heat transfer coefficient, (kW/m²·K)
- V bulk fluid velocity, (m/s)

friction velocity = $\sqrt{\tau_w / \rho} = V \sqrt{f / 2}$, (m/s) v.

- deposit thickness, (m) X_f
- axial location along length of test section, (mm) Z

Greek Letters

- fluid dynamic viscosity, (kg/m·s) η
- thermal conductivity, (kW/m·K) λ
- fluid density, (kg/m³) ρ
- Fouling deposit density, (kg/m³)
- $\rho_t \ \sigma^2$ sample variance, (m²·K/kj)²
- shear stress at wall, (Pa) τ.,,

Subscripts

- b bulk
- c clean f foulant
- i inside
- o initial
- w wall

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