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NOVEL APPROACHES CONCERNING CATALYST DEACTIVATION

Research Period Covered July 1, 1982–December 31, 1983

By
T. T. Tsotsis

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University of Southern California
Los Angeles, California

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Final Report

NOVEL APPROACHES CONCERNING
CATALYST DEACTIVATION

Department of Chemical Engineering
University of Southern California
Los Angeles, CA 90089-1211

Research Period Covered

July 1, 1982 - Dec. 31, 1983

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INTRODUCTION

During the second year of this project attention has been focused on problems of deactivation by site coverage and pore blockage which follow series-type kinetic expressions. This study has not been completed at the time this final report was submitted and what is presented here is the results of the part of this study completed by December 31, 1983. The first part of this final report is devoted to the reexamination of a model suggested recently by Wei and Wei [1] to model deactivation phenomena during hydroprocessing and hydro-demetallation of coal and heavy petroleum derived oils. This model assumes quasi-stationary conditions and does not include an apparent mechanism for site coverage and pore blockage. It was decided, however, that a closer look and reexamination of this model was needed, since it describes the initial state of more complete deactivation models and the phenomenon of deactivation for short process times, is amenable to analytical solutions and qualitatively predicts all the possible metal profiles one expects to find on spent catalysts that have been deactivated by series-type deactivation mechanisms. This final report does not include the results presented in our first two quarterly reports. Furthermore, no additional discussion of the current literature is included since an extensive literature survey can be found in our second quarterly report and in two upcoming publications (2,3).

The second part of this final report contains a description of the complete deactivation model currently under investigation. Results of this study will be presented in the upcoming AIChE national meeting.

A. A SIMPLE MODEL OF DEACTIVATION BY SERIES TYPE KINETICS

(I) The Model

An extensive discussion of the development of this model can be found in [1]. The deactivation mechanism can be described as

where A is the heavy oil (residual oil from the bottom of refinery distillation columns or coal derived liquid) to be hydro-demetalated (or hydroprocessed)) B an intermediate (possibly a hydrogenated form of A) and C the metal (or other deposit) deposited on the catalyst. The main assumptions involved in this model are that (1) quasi-stationary conditions prevail throughout the whole process (2) C is strongly held on the catalyst surface and not allowed to diffuse through the catalyst pore structure and (3) that deposition of C has no appreciable effect on the catalyst activity and pore structure. Assumptions (1) and (3) are questionable (especially 3) and contradictory to currently available experimental data.

The model presented in part B of this report does not make use of assumptions (1) and (3). The goals in part A of this report are basically similar with those of the original publication [1] i.e., to investigate all the different possible metal profiles that the model predicts can be found in spent hydro-demetallation catalysts. A set of analytical criteria is presented predicting the different metal profiles (something that was not done in the original publication). Furthermore, all the different types of catalytic reactor behavior possible, when the hydro-demetallation (HDM) reaction is carried out in tubular (packed-bed) reactors, have been investigated.

(II) The Single Catalyst Particle

In this chapter the model proposed in [1] is studied. This model describes the behavior of a single (or a bed of) catalyst in a differential CSTR. Liquid phase mass transfer limitations are assumed to be negligible and the whole process is assumed to be isothermal. In view of these assumptions (and the assumptions of chapter (I), see also ref. 1) the model equations for a slab catalyst particle are

$$\bar{D} \nabla^2 \bar{C} = \bar{K} \bar{C} \quad (2a)$$

$$\left. \frac{\partial \bar{C}}{\partial X} \right|_{X=0} = 0 \quad (2b)$$

$$\bar{C} \Big|_{X=R} = \bar{C}_0, \quad (2c)$$

where

$$\bar{D} = \begin{bmatrix} D_A & 0 \\ 0 & D_B \end{bmatrix}, \quad \bar{K} = \rho_p S_g \begin{bmatrix} K_1 & -K_2 \\ -K_1 & K_2 + K_3 \end{bmatrix}$$

$$\bar{C} = \begin{bmatrix} C_A \\ C_B \end{bmatrix}, \quad \bar{C}_0 = \begin{bmatrix} C_{A0} \\ C_{B0} \end{bmatrix}$$

By defining the following dimensionless symbols

$$\mathcal{L} = \frac{K_2}{K_1}, \quad \mathcal{E} = \frac{D_A}{D_B}$$

$$\beta = \frac{K_3}{K_1}, \quad \phi = L \sqrt{\frac{K_1 P_p S_g}{D_A}}$$

$$\gamma = \frac{C_{B0}}{C_{A0}}, \quad \xi = \frac{x}{R}$$

$$\bar{Y} = \begin{bmatrix} \bar{C} \\ C_{A0} \end{bmatrix}, \quad A = \begin{bmatrix} 1 & 0 \\ 0 & \varepsilon \end{bmatrix} \begin{bmatrix} 1 & -\alpha \\ -1 & \alpha + \beta \end{bmatrix}$$

equation (2) becomes

$$V^2 \bar{Y} = \phi^2 \bar{A} \bar{Y} \quad (3a)$$

$$\left. \frac{\partial \bar{Y}}{\partial \xi} \right|_{\xi=0} = \bar{0} \quad (3b)$$

$$\bar{Y} \Big|_{\xi=1} = \begin{bmatrix} 1 \\ \gamma \end{bmatrix} \quad (3d)$$

Equations (3) of course admit an analytical solution

$$\bar{Y} = \bar{G} \begin{bmatrix} \frac{\cosh \phi T \bar{\lambda}_1 \xi}{\cosh \phi T \bar{\lambda}_1} & 0 \\ 0 & \frac{\cosh \phi T \bar{\lambda}_2 \xi}{\cosh \phi T \bar{\lambda}_2} \end{bmatrix} \bar{G}^{-1} \begin{bmatrix} 1 \\ \gamma \end{bmatrix}, \quad (4)$$

where $\bar{G}$ is the eigenvector matrix and λ_1, λ_2 the eigenvalues of $\bar{A}$.

λ_1 and λ_2 are given as:

$$\lambda_{1,2} = \frac{\varepsilon(\alpha + \beta) + 1 \pm \sqrt{\varepsilon(\alpha + \beta + 1)^2 - 4\varepsilon\beta}}{2} \quad (5)$$

and if one assumes that $\lambda_1 > \lambda_2$ then it can be shown that

$$\lambda_1 > 1 > \lambda_2 > 0 \quad (6)$$

Note that since species C stays localized and not allowed to diffuse the local concentration profiles of C (metal profiles) are similar to those of B (i.e., Y_2). In view of Equation (3b) a necessary (but not sufficient) condition for the existence of a maximum of Y_2 in $[0,1]$ is

$$\left. \frac{d^2 Y_2}{d\xi^2} \right|_{\xi=0} \geq 0 \quad (7)$$

Three different concentration profiles for Y_2 , are possible (shown in Fig. 1). The necessary and sufficient conditions for the existence of each one of these profiles are

$$\text{TYPE 2: } \left. \frac{dY_2}{d\xi} \right|_{\xi=1} \geq 0 \quad (8a)$$

$$\text{TYPE 1: } \left. \frac{dY_2}{d\xi} \right|_{\xi=1} \leq 0 \quad \text{and} \quad \left. \frac{d^2 Y_2}{d\xi^2} \right|_{\xi=0} \geq 0 \quad (8b)$$

$$\text{TYPE 0: All other cases not covered by Equations (8) and (9)} \quad (8c)$$

Fig. 1 Different types of metal profiles found on spent catalysts.

Note that

$$\frac{dY_2}{d\xi} = \frac{\phi}{\lambda(\lambda_1 - \lambda_2)} \left[\frac{\sqrt{\lambda_1}(1-\lambda_1)(1-\lambda_2-\alpha\gamma) \sinh \phi \sqrt{\lambda_1} \xi}{\cosh \phi \sqrt{\lambda_1}} - \right. \quad (9)$$

$$\left. \frac{\sqrt{\lambda_2}(1-\lambda_2) - (1-\lambda_1-\alpha\gamma) \sinh \phi \sqrt{\lambda_2} \xi}{\cosh \phi \sqrt{\lambda_2}} \right] = F_1(\phi, \xi)$$

$$\frac{d^2 Y_2}{d\xi^2} = \frac{\phi^2}{\lambda(\lambda_1 - \lambda_2)} \left[\frac{\lambda_1(1-\lambda_1)(1-\lambda_2-\alpha\gamma) \cosh \phi \sqrt{\lambda_1} \xi}{\cosh \phi \sqrt{\lambda_1}} - \frac{\lambda^2}{\cosh \phi \sqrt{\lambda_2}} - \right. \quad (10)$$

$$\left. (1-\lambda_2)(1-\lambda_1-\alpha\gamma) \cosh \phi \sqrt{\lambda_2} \xi \right] = F_2(\phi, \xi)$$

Define as $\phi_{\min}$ the solution of

$$F_2(\phi, 0) = 0$$

and as $\phi_{\max}$ the solution of

$$F_2(\phi, 1) = 0 \quad (12)$$

Then conditions (8) are equivalent to the following set of conditions.

$$\text{TYPE 2: } \phi \geq \phi_{\max} \quad (13a)$$

$$\text{TYPE 1: } \phi_{\min} < \phi < \phi_{\max} \quad (13b)$$

$$\text{TYPE 0: } \phi \leq \phi_{\min} \quad (13c)$$

In Fig. 2 $\phi_{\min}$ and $\phi_{\max}$ are plotted versus γ . There is a critical value of γ (γ_{cr}) below which $\phi_{\max}$ does not exist and only profiles 0 and 1 are possible. There is another critical value of γ (γ^{cr}) above which $\phi_{\min}$ and $\phi_{\max}$ are both zero and only profile 2 is possible. Note, furthermore, that as γ decreases from γ^{cr} , $\phi_{\max}$ very rapidly approaches an asymptotic value.

One can view the results shown in Fig. 2 from several points of view. For a CSTR differential reactor an increase in γ is accomplished by an increase in the product stream recycle ratio. If therefore one deals with a catalytic system for which $\phi < \phi_{\min}^{\text{cr}}$ ($\phi_{\min}^{\text{cr}}$ is the value of $\phi_{\min}$ corresponding to $\gamma = 0$) as the recycle ratio is increased there is a smooth transition between metal profiles of type 0 to 1 to 2. Above $\phi_{\min}^{\text{cr}}$ of course profile 0 is not possible anymore and there is only a transition between profiles 1 to 2.

As α increases both γ_{cr} and γ^{cr} as well as $\phi_{\min}^{\text{cr}}$ decrease (see Fig. 3). The same is also true when β increases (see Fig. 4).

If the assumption that G does not affect catalytic activity is relaxed and instead one assumes that the catalytic activity is slowly decreasing as a function of time then Figs. 2, 3 and 4 predict a rich variety of catalytic behavior. If at the start of the hydro-demetalation process $\phi < \phi_{\min}$ and $\gamma < \gamma_{\text{cr}}$ then the only metal profile one expects to find on spent catalysts is profile 0. If on the other hand at the start of the process $\phi > \phi_{\min}$ and $\gamma < \gamma_{\text{cr}}$ then as process time increases one expects a gradual change from profile type 1 to profile type 0. All the different types of catalytic behavior one expects to find in this case are shown in Table 1.

If the metal deposition also affects the catalyst pore structure and therefore decreases the effective diffusion coefficient very complex behavior is possible since ϕ can first decrease and then increase and then decrease again. Such complex behavior has been predicted from the analysis of the

Fig. 2 $\phi_{\min}$, $\phi_{\max}$ versus γ . $\varepsilon = 1$, $\alpha = 1$, $\beta = .1$

Fig. 3 $\phi_{\min}$, $\phi_{\max}$ versus γ , $\varepsilon = 1$, $\alpha = 4$, $\beta = 0.1$

Fig. 4 $\phi_{\min}$, $\phi_{\max}$ versus γ , $\epsilon = 1$, $\alpha = 1$, $\beta = 1$.

complete deactivation model of part B of this final report.

TABLE 1

CASE No.	INITIAL CONDITIONS	CATALYTIC BEHAVIOR AS PROCESS TIME INCREASES
1	$\phi < \phi_{min}$	0
2	$\gamma_{cr} < \gamma < \gamma^{cr}, \phi_{min} < \phi < \phi_{max}$	$1 \rightarrow 0$
3	$\gamma_{cr} < \gamma < \gamma^{cr}, \phi > \phi_{max}$	$2 \rightarrow 1 \rightarrow 0$
4	$\gamma > \gamma^{cr}$	2

(III) The Tubular Reactor Problem

In this chapter it is assumed that the hydro-demetalation reaction is carried out under isothermal conditions in a tubular (packed-bed) reactor.

The reactor design equations (pseudo-homogeneous mode) are

$$U \frac{\partial C_A^g}{\partial z} = -E_b r_{PA} \quad (14a)$$

$$U \frac{\partial C_B^g}{\partial z} = E_b r_{PB} \quad (14b)$$

$$z=0 \quad ; \quad C_A^g = C_{A0}^g \quad ; \quad C_B^g = C_{B0}^g \quad (14c)$$

$$r_{PA} = K_1 \rho_p S_g n_{PA} C_A^g ; \quad r_{PB} = K_1 \rho_p S_g n_{PB} C_A^g \quad (14d)$$

$$n_{PA} = \frac{\partial Y_1}{\partial \xi} \bigg|_{\xi=1} / \phi^2 \quad (14e)$$

$$n_{PB} = - \varepsilon \frac{\partial Y_2}{\partial \xi} \bigg|_{\xi=1} / \phi^2 \quad (14f)$$

Y_1, Y_2 are of course the solutions of Equation (3), and the remaining symbols are defined in the Nomenclature Appendix. Equations are made dimensionless by defining

$$X_1 = \frac{C_A^g}{C_{AO}^g} ; \quad X_2 = \frac{C_B^g}{C_{AO}^g} , \quad p = \frac{\varepsilon_b L K_1}{u} ,$$

$$\psi = \frac{z}{L} , \quad \gamma_0 = \frac{C_{BO}^g}{C_{AO}^g}$$

as follows,

$$\frac{\partial X_1}{\partial \psi} = - p n_{AP} X_1 \quad (15a)$$

$$\frac{\partial X_2}{\partial \psi} = p n_{PB} X_2 \quad (15b)$$

$$\psi = 0 ; \quad X_1 = 1 ; \quad X_2 = \gamma_0 \quad (15c)$$

From the definition of γ in chapter (II) and of X_1 and X_2 above

$$\gamma = \frac{X_2}{X_1} \quad (16)$$

Since, of course, X_1 and X_2 are functions of Ψ , γ is also a function of Ψ . From Equation (9)

$$\left. \frac{dY_2}{d\xi} \right|_{\xi=1} = B_2(\lambda_1, \lambda_2, \phi) + \gamma E_2(\lambda_1, \lambda_2, \phi), \quad (17)$$

where

$$B_2(\lambda_1, \lambda_2, \phi) = \frac{\phi(1-\lambda_1)(1-\lambda_2)}{\lambda_1 - \lambda_2} \left[T\lambda_1 \tanh \phi T\lambda_1 - T\lambda_2 \tanh \phi T\lambda_2 \right] \quad (18a)$$

$$E_2(\lambda_1, \lambda_2, \phi) = \frac{\phi}{(\lambda_1 - \lambda_2)} \left[T\lambda_2(1-\lambda_2) \tanh \phi T\lambda_2 - T\lambda_1(1-\lambda_1) \tanh \phi T\lambda_1 \right] \quad (18b)$$

Similarly

$$\left. \frac{dY_1}{d\xi} \right|_{\xi=1} = B_1(\lambda_1, \lambda_2, \phi) + \gamma E_1(\lambda_1, \lambda_2, \phi), \quad (19)$$

where

$$B_1(\lambda_1, \lambda_2, \phi) = \frac{\phi}{\lambda_1 - \lambda_2} \left[T\lambda_1(1-\lambda_2) \tanh \phi T\lambda_1 - T\lambda_2(1-\lambda_1) \tanh \phi T\lambda_2 \right] \quad (20a)$$

$$E_1(\lambda_1, \lambda_2, \phi) = \frac{\phi}{\lambda_1 - \lambda_2} \left[T\lambda_2 \tanh \phi T\lambda_2 - T\lambda_1 \tanh \phi T\lambda_1 \right] \quad (20b)$$

Equation (15) then becomes

$$\frac{d}{d\psi} \begin{bmatrix} X_1 \\ X_2 \end{bmatrix} = \bar{B} \begin{bmatrix} X_1 \\ X_2 \end{bmatrix} \quad (21a)$$

where

$$\bar{B} = \frac{\rho}{\phi^2} \begin{bmatrix} B_1 & E_1 \\ -B_2/\varepsilon & -E_2/\varepsilon \end{bmatrix} \quad (21b)$$

If σ_1, σ_2 are the eigenvalues of $\bar{B}$ and $\psi' = \psi\rho/\phi^2$ then X_1 and X_2 are given as

$$X_1 = \frac{\sigma_1 e^{\sigma_2 \psi'} - \sigma_2 e^{\sigma_1 \psi'}}{\sigma_1 - \sigma_2} - \frac{B_1 + \varepsilon_1 \gamma_0}{\sigma_1 - \sigma_2} (e^{\sigma_2 \psi'} - e^{\sigma_1 \psi'}) \quad (22a)$$

$$X_2 = \gamma_0 \frac{\sigma_1 e^{\sigma_2 \psi'} - \sigma_2 e^{\sigma_1 \psi'}}{\sigma_1 - \sigma_2} - \frac{1}{\varepsilon} \frac{(B_2 + \gamma_0 \varepsilon_2)}{\sigma_1 - \sigma_2} (e^{\sigma_1 \psi'} - e^{\sigma_2 \psi'}) \quad (22b)$$

Define as γ_f the value of (X_2/X_1) at the reactor outlet stream. For large P (large reactor space times) γ_f tends to an asymptotic value, which is independent of γ_0 and is given by the following equation

$$\gamma_f^\infty = \lim_{P \rightarrow \infty} \gamma_f = \frac{B_2/\varepsilon}{\rho_2 - B_1} \quad (23)$$

This limiting γ_f value is plotted in Fig. 5 together with γ^{cr} and γ_{cr} as a function of ϕ for different sets of values of parameters α , β and ϵ . Note that for large values of ϕ , γ_f^∞ approaches an asymptotic value. Note also that $\gamma_f^\infty < \gamma^{cr}$ for all values of ϕ and that there is a critical value of ϕ (defined as ϕ_{cr}) above which $\gamma_f^\infty < \gamma_{cr}$.

By utilizing Equations (2) and (22) as well as the definitions of ϕ_{min} and ϕ_{max} one can again predict the different metal profiles that prevail at each point in the reactor. The results of this study are presented in Figs. 6a and 6b, where the dimensionless reactor length, where each of the different metal profile types (0, 1 and 2) can be found, is plotted versus ϕ .

The behavior shown in Fig. 6 is quite interesting. Let us first focus attention on Fig. 6a for the case when $\gamma = 0.6$. Note that for small values of ϕ all three types of metal profiles can be found inside the reactor although profiles 1 and 2 can be found in only a small region at the inlet of the reactor. As ϕ increases the inlet reactor region where profiles 1 and 2 prevail increases until a critical value of ϕ beyond which profile 0 is not possible anymore. For $\gamma_0 = 0.4$ for small values of ϕ only profile 0 is possible. As ϕ increases there is a region of ϕ values where profiles 1 and 0 are possible and for larger values of ϕ a region where only profiles 2 and 1 are possible. The different types of behavior shown in Fig. 6 strongly depend on the size of γ_0 and the values of P which determines the reactor conversion of the value of γ at the reactor exit i.e., γ_f . Given a large value of P (which is equivalent to saying given a large reactor space time) the different types of reactor behavior possible (for constant α , β , ϵ values) are summarized in Table 2 and Fig. 7.

As it can be seen in Fig. 7 the behavior of the reactor can be described in

a

b

c

d

Fig. 5 γ_f^∞ versus ϕ . (a) $\alpha = 1, \beta = 1, \epsilon = 1$ (b) $\alpha = 4, \beta = 1, \epsilon = 1$
(c) $\alpha = 1, \beta = 0.2, \epsilon = 1$ (d) $\alpha = 1, \beta = 1, \epsilon = 0.5$

a

b

Fig. 6 Reactor length $\%$ where the different metal profiles are found.

$$\alpha = 1, \beta = 1, \epsilon = 1, P = 5$$

terms of the three curves $\phi_{\min}(\gamma)$, $\phi_{\max}(\gamma)$ and $\gamma_f^{\infty}(\phi)$.

Note that the qualitative relative location of the three curves with respect to each other as well as with respect to the asymptotic values $\gamma = \gamma_{cr}$ and $\gamma = \gamma^{cr}$ is the same for all the possible values of α , β , ϵ .

Table 2 lists all the different types of behavior in terms of metal profiles on spent catalysts found in the reactor as a function of ϕ and γ_0 (for constant values of α , β and ϵ). Note that the parameter ϕ_{cr} used in Table 2 is the value of ϕ corresponding to the intersection of curves $\phi_{\min}(\gamma)$ and $\gamma_f^{\infty}(\phi)$.

Table 2

CASE	CONDITION ON ϕ	CONDITION ON γ_0	BEHAVIOR OF THE REACTOR FROM THE ENTRANCE TO THE EXIT PROFILE TYPE
1a	$\phi < \phi_{cr}$	$\gamma_0 > \gamma(\phi_{max} = \phi)$	① "2" → "1" → "0"
1b	$\phi < \phi_{cr}$	$\gamma(\phi_{min} = \phi) < \gamma_0 < \gamma(\phi_{max} = \phi)$	"1" → "0"
1c	$\phi \leq \phi_{cr}$	$\gamma_0 < \gamma(\phi_{min} = \phi)$	② "0"
2a	$\phi \geq \phi_{cr}$	$\gamma_0 > \gamma(\phi_{max} = \phi)$	① "2" → "1"
2b	$\phi \geq \phi_{cr}$	$\gamma_{fired}(\phi) < \gamma < \gamma(\phi_{max} = \phi)$	"1"
2c	$\phi_{min}(\phi) \geq \phi > \phi_{cr}$	$\gamma < \gamma(\phi_{min} = \phi)$	"0" → "1"
2d	$\phi > \phi_{cr}$	$\gamma_{fired}(\phi) > \gamma > \gamma(\phi_{min} = \phi)$	③ "1"

- ① ALWAYS TRUE FOR $\gamma_0 > \gamma^{cr}$
 ② ALWAYS TRUE FOR $\gamma_0 < \gamma_{cr}$
 ③ ALWAYS TRUE FOR $\phi > \phi_{min}$

Note that in general if $\phi < \phi_{cr}$ the profile at the reactor exit will be of type '0', and if $\phi > \phi_{cr}$ the profile at the reactor exit will be of type '1'.

Fig. 7 Schematic figure showing the different types of reactor behavior possible for $P \rightarrow \infty$.

For smaller values of P for which complete conversion is not possible a richer variety of catalytic reactor behavior is to be expected.

If one again assumes that metal deposition results in a slow catalytic activity decline then many interesting types of catalytic reactor behavior are possible. As an illustrative example let us consider for example the case of Fig. 6a where $\phi = 4$ and $\gamma = 0.6$. As the activity declines slowly the inlet reactor region, where profile 2 (for a large value of P) prevails, decreases with a corresponding increase in the reactor region, where profile 1 prevails. Experimentally this would of course appear as a backwards propagating metal profile wave. At some point, while the region with profile type 2 is still receding, at the outlet of the reactor a region will appear which contains metal profiles of type 0. At this point, experimentally one would observe two backwards propagating metal profile waves.

For smaller values of P or for the case that metal deposition also affects the catalytic pore structure the catalytic reactor behavior can be very complex.

B. THE COMPLETE DEACTIVATION MODEL

What is presented here is the description of the complete deactivation model still under investigation. The numerical techniques utilized in the analysis of this problem and initial results of this analysis can be found in [4]. The equations describing a single catalyst deactivating by site coverage and pore blockage and by a series type deactivation mechanism (Equation 1) are

$$\frac{\partial(\epsilon \rho C_A)}{\partial t} = \frac{\partial}{\partial x} \left(D_{AC} \frac{\partial C_A}{\partial x} \right) - K_1 \rho_p S_g W_{MT} \left(1 - \frac{W_M}{W_{MT}} \right) C_A + K_2 \rho_p S_g W_{MT} \left(1 - \frac{W_M}{W_{MT}} \right) C_B \quad (24a)$$

$$\frac{\partial(\epsilon_p C_B)}{\partial t} = \frac{\partial}{\partial x} \left(D_{BE} \frac{\partial C_B}{\partial x} \right) - K_2 \rho_p S_g W_{MT} \left(1 - \frac{W_M}{W_{MT}} \right) C_B + K_1 \rho_p S_g W_{MT} \left(1 - \frac{W_M}{W_{MT}} \right) C_A \quad (24)$$

$$+ K_3 \rho_p S_g W_{MT} \left(1 - \frac{W_M}{W_{MT}} \right) C_B$$

$$\frac{\partial W_M}{\partial t} = K_3 \rho_p S_g W_{MT} \left(1 - \frac{W_M}{W_{MT}} \right) C_B \quad (24c)$$

Initial conditions:

$$t = 0 ; \quad W_M = 0 ; \quad C_A = 0 ; \quad C_B = 0 \quad (24d)$$

Boundary conditions:

$$x = 0 ; \quad \frac{\partial C_A}{\partial x} = \frac{\partial C_B}{\partial x} = 0 \quad (24e)$$

$$x = R ; \quad C_A = C_{A0} ; \quad C_B = C_{B0} \quad (24f)$$

W_M is the local metal density (per gr. of catalyst), which can of course be measured by a variety of modern surface techniques. The only assumption involved in these equations (besides the assumption of pseudo-first order kinetics) is that the activity decline due to metal deposition can be

expressed as a linear function of the local metal concentration. In accordance with other recent investigation, it is further assumed that

$$\epsilon_p = \epsilon_{p0} - W_m \left(\frac{\rho_p}{\rho_m} \right), \quad (25)$$

where $\epsilon_{p0}, \epsilon_p$ are the initial and local catalyst porosities and ρ_p, ρ_m are the densities of the particle and of the metal deposit. It is assumed that the deposited metal also affects the local diffusivity according to the semi-empirical relationship developed initially by Satterfield [5] and utilized recently in several other publications [6, 7].

$$D_{ie} = D_{i0} \epsilon_p F(\delta_i) \quad i = A, B \quad (26a)$$

$$\delta_i = \delta_{i0} \left(\frac{\epsilon_{p0}}{\epsilon_{pi}} \right)^{1/2} \quad (26b)$$

$$F(\delta_i) = \exp(-4.6 \delta_i) \quad \text{if } \delta_i < 1 \quad (26c)$$

$$F(\delta_i) = 0 \quad \text{if } \delta_i \geq 1 \quad (26d)$$

By defining

$$\Phi = R \sqrt{\frac{K_1 \rho_p S_0 W_{MT}}{D_{A0} \epsilon_{p0}}}, \quad Y_1 = \frac{C_A}{C_{A0}}, \quad Y_2 = \frac{C_B}{C_{B0}}, \quad Y_3 = \frac{W_m}{W_{MT}},$$

$$\xi = \frac{x}{R}, \quad \epsilon = \frac{D_{B0}}{D_{A0}}, \quad \alpha = \frac{K_2}{K_1}, \quad \beta = \frac{K_3}{K_1},$$

$$\epsilon'_p = \frac{\epsilon_p}{\epsilon_{p0}}, \quad \theta = \frac{t L^2}{D_{A0}} \cdot \frac{W_{MT}}{C_{A0}} \cdot \frac{1}{B \Phi^2}, \quad \gamma = \frac{C_{B0}}{C_{A0}}$$

Equations (26) become

$$\gamma_1 \frac{\partial}{\partial \theta} (\varepsilon_p' \gamma_1) = \frac{\partial}{\partial \xi} \left(\varepsilon_p' \frac{\partial \gamma_1}{\partial \xi} \right) - \phi^2 (1 - \gamma_3) (\gamma_1 - \alpha \gamma_2) \quad (27a)$$

$$\gamma_1 \frac{\partial}{\partial \theta} (\varepsilon_p' \gamma_2) = \frac{\partial}{\partial \xi} \left(\varepsilon_p' \frac{\partial \gamma_2}{\partial \xi} \right) - \phi^2 (1 - \gamma_3) [(\alpha + \beta) \gamma_2 - \gamma_1] \quad (27b)$$

$$\frac{\partial \gamma_3}{\partial \theta} = (1 - \gamma_3) \gamma_2, \quad (27c)$$

where

$$\gamma_1 = \frac{C_{AD}}{W_{MT}} \cdot \phi^2 \cdot \beta.$$

Initial conditions

$$\theta = 0 \quad ; \quad \gamma_1 = 0 \quad ; \quad \gamma_2 = 0 \quad ; \quad \gamma_3 = 0 \quad (27d)$$

Boundary conditions

$$\xi = 0 \quad ; \quad \frac{\partial \gamma_1}{\partial \xi} = \frac{\partial \gamma_2}{\partial \xi} = 0 \quad (27e)$$

$$\xi = 1 \quad ; \quad \gamma_1 = 1 \quad ; \quad \gamma_2 = 0, \quad (27f)$$

where

$$\varepsilon_p' = 1 - b \gamma_3 \quad (28a)$$

$$b = \frac{W_{MT}}{\varepsilon_{p0}} \left(\frac{\rho_p}{\rho_m} \right) \quad (28b)$$

For the case, where the hydro-demetalation reaction is carried out in a tubular packed-bed reactor, the set of Equations (27) is complemented by the design equations for the tubular reactor (equations 17).

The analysis of the set of equations (28) has yet to be completed and is not presented in this report.

CONCLUDING REMARKS

What is presented here is the complete analysis of a model originally suggested by Wei and Wei (1) to model the behavior of catalysts during hydro-demetalation of coal derived liquids.

This model does not take into account the fact that as hydro-demetalation reaction proceeds the deposited metals deactivate the catalyst and destroy its pore structure. It was felt however that a complete analysis of this model was needed since it is amenable to analytical solutions, describes the initial state of more complete deactivation models and qualitatively predicts all the different metal profiles one expects to find on spent (deactivated) catalysts.

We have also presented here the set of equations describing a more complete and "realistic" hydro-demetalation model. The analysis of this model; however has yet to be completed and will be presented later as an "addendum" to this report.

BIBLIOGRAPHY

1. J. Wei and R. G. Wei, 'Metal Deposition Profiles in Hydro-Demetallation', Chem. Eng. Comm., 13, 251, 1982.
2. Y. C. Yortsos and T. T. Tsotsis, 'A Model Case of Deactivation By Site Coverage and Pore Blockage', to appear in Chem. Eng. Comm.
3. K. Tsakalis, T. T. Tsotsis and G. J. Steigel, 'Deactivation Phenomena By Site Coverage and Pore Blockage. The Effect of Catalyst Size, Pore Size and Pore Size Distribution', to appear in J. of Catal.
4. K. Tsakalis, 'Deactivation Phenomena by Site Coverage and Pore Blockage', M.S. Thesis, Dept. of Chem. Engineering, U. S. C., Los Angeles, CA 1984.
5. C. N. Satterfield, C. K. Colton and U. J. Pitcher, 'Restricted Diffusion in Liquids with Fine Pores', AIChE J., 19, 628, 1973.
6. M. J. Chiou and J. H. Olson, 'Effect of Catalyst Pore Structure on the Hydroprocessing of Coal Derived Liquids', ACS Symp. Ser., 23, 1421, 1978.
7. H. J. Chang, M. Seapan and B. L. Crynes, 'Catalyst Decay During Hydrotreatment of Heavy Coal Oils', ACS Symp. Ser., 196, 309, 1981.

LIST OF SYMBOLS

$\bar{A}$	the matrix of dimensionless reaction constants and diffusivity defined as $\begin{bmatrix} 1 & 0 \\ 0 & \end{bmatrix} \begin{bmatrix} 1 & -\alpha \\ -1 & \alpha + \beta \end{bmatrix}$
$\bar{B}$	the matrix of the differential equations for the reactor problem defined in Equation 21b.
b	coke size parameter defined in Equation 28b.
B_i	coefficients of the matrix $\bar{B}$ defined in Equations 18a and 20a.
C_i	concentration of species i in the catalyst
C_{i0}	concentration of species i at the catalyst liquid interface
C_i^g	concentration of species i at the gas phase
$\bar{C}$	concentration vector $\begin{bmatrix} C_A \\ C_B \end{bmatrix}$
$\bar{C}_0$	concentration vector at the catalyst liquid interface
D_i	diffusivity of species i
D_{i0}	bulk diffusivity of species i
D_{ie}	effective diffusivity of species i
$\bar{D}$	the diffusivity matrix $\begin{bmatrix} D_A & 0 \\ 0 & D_B \end{bmatrix}$
E_i	coefficients of matrix $\bar{B}$ defined in Equations 18b and 20b
k_i	reaction constants
$\bar{K}$	the matrix of reaction constants $\rho_p^S \varepsilon \begin{bmatrix} k_1 & -k_2 \\ -k_1 & k_2 + k_3 \end{bmatrix}$
L	length of reactor
P	dimensionless reactor length = $\frac{\varepsilon_b L k_1}{u}$

r_{pi}	reaction rate for species i per unit volume
R	half length of catalyst
S_g	surface area per unit weight
t	time
u	reactor space velocity
W_M	density of metal deposits (gr. of metal per gr. of catalyst)
W_{MT}	density of metal deposits when all sites are covered by metal
X	catalyst length variable
X_i	dimensionless concentration of species i in the reactor gas phase
Y_i	dimensionless concentration of species i in the catalyst pore
Z	reactor length variable
α	equilibrium constant k_2/k_1
β	ratio of reaction rate constants k_3/k_1
γ	ratio of concentrations X_2/X_1
γ_0	the ratio X_2/X_1 at the inlet of the reactor
γ_{cr}	the minimum value of γ for which ϕ_{max} is finite
γ^{cr}	the maximum value of γ for which ϕ_{min} , ϕ_{max} are nonzero
γ_f	the value of X_2/X_1 at the reactor outlet
γ_f^∞	the limit value of γ_f for infinite P
γ_1	constant $(C_{Ao}/W_{MT})\phi^2 \cdot B$
δ_i, δ_{i0}	pore size parameters defined by Equation (26)
ϵ	ratio of diffusivities $\epsilon = D_A/D_B$
ϵ_b	porosity of bed
ϵ_p	local porosity in catalyst

η_{pi}	effectiveness factor for species i
θ	dimensionless time $(tL^2/D_{AO})(W_{MT}/C_{AO})(1/\beta\phi^2)$
$\lambda_{1, 2}$	eigenvalues of matrix $\bar{A}$
ϵ	dimensionless catalyst length
ρ_p	density of catalyst
$\sigma_{1, 2}$	eigenvalues of matrix $\bar{B} \cdot \phi^2 / p$
ϕ	Thiele modulus $R \cdot \sqrt{\frac{k_1 \rho_p S_g W_{MT}}{D_{AO}}}$
ϕ_{min}	minimum Thiele modulus for which profile type '2' occurs
ϕ_{max}	minimum Thiele modulus for which profile type '1' occurs
ϕ_{min}^{cr}	the value of ϕ_{min} correspondent to $\gamma = 0$
Ψ	dimensionless reactor length, z/L
Ψ'	modified dimensionless reactor length, $\Psi P / \phi^2$