APPENDIX B

CALCULATIONS OF THEORETICAL CRITERIA FOR DIFFUSION EFFECTS

Theoretical Criterion for Concentration Gradient inside Catalyst Particle

For a porous solid, a mean pore radius, r_e, can be defined as [189]:

$$r_e \equiv \frac{2V_g}{A_p} = \frac{2\theta}{A_p \rho_p} \qquad (B.1)$$

where V_g is the pore volume per unit mass of catalyst, in cm^3/gm, A_p is the total surface area per unit mass of porous catalyst, in cm^2/gm, ρ_p is the pellet density, in gm/cm^3, and θ is the porosity of catalyst.
Assume that the geometry of the catalyst can be approximated by its major constituent support, i.e., ALCOA F-1 activated alumina (100 mesh), from vender info $V_g = 0.40\ cm^3/gm$, $A_p = 250\ m^2/gm$, $\rho_p = 1.42\ gm/cm^3$ and $\theta = 0.563$. Plugging all these values into Eqn. (B.1) gives

$$r_e = \frac{2(0.40\ cm^3/gm)}{(250\ m^2/gm)(10^4\ cm^2/m^2)}$$

$$= 3.20\text{x}10^{-7}\ cm.$$

For Knudsen diffusion in gases in a straight cylindrical pore, the Knudsen diffusivity, D_K, can be calculated [189],

$$D_K = 9700 r_e \sqrt{\frac{T}{M}} \qquad (B.2)$$

where T is the temperature, in degrees Kelvin and M is the molecular weight.

Refer to the typicl material balance in Appendix H, $M = M_{\text{gas product}} = 21.68$ gm/mol, hence

$$D_K = 9700(3.20\text{x}10^{-7}\ \text{cm})\sqrt{\frac{494.26\ \text{K}}{21.68\ \text{gm/mol}}}$$

$$= 0.0148\ \text{cm}^2/\text{s}.$$

For a porous solid, the Knudsen diffusivity becomes

$$D_{K,eff} = \frac{D_K \theta}{\tau_{r_e}} \qquad (B.3)$$

where τ_{r_e} is the tortuosity, an empirical factor obtained assuming completely Knudsen diffusion and the mean pore radius defined by Eqn. (B.1), and is usually taken a value of 4.

$$D_{K,eff} = \frac{(0.0148\ cm^2/s)(0.563)}{4}$$

$$= 0.0021\ cm^2/s.$$

For multicomponent gas mixture, an alternate effective binary diffusivity with the flux, N_j, of bulk diffusion of component j relative to the fixed solid can be defined

$$N_j \equiv -C_s D_{jm} \nabla y_j \qquad (B.4)$$

where C_s is total molar concentration of active sites, in mol/gm cat., D_{jm} is effective molecualr diffusivity of component j in a multicomponent mixture, y_j is mole fraction of species j and ∇ is the mathematical operator of vector differentiation.

Assume N_j = 0 (for dilute j), then Eqn. (B.4) can lead to

$$D_{jm} = \Big(\sum_{\substack{i=1 \\ i \neq j}}^{n} \frac{y_i}{D_{ji}} \Big)^{-1} \qquad (B.5)$$

Let j = 3 representing ethylene, and i = 1, 2, 4, 5 and 6 designating hydrogen, carbon monoxide, carbon dioxide, methane and ethane respectively.

An empirical correlation suggested by Fuller, Schettler and Giddings is used to calculate the pseudo binary diffusivities [180]:

$$D_{ji} = \frac{10^{-3} T^{1.75} \left(\frac{1}{M_j} + \frac{1}{M_i}\right)^{\frac{1}{2}}}{P\{(\Sigma\upsilon)_j^{\frac{1}{3}} + (\Sigma\upsilon)_i^{\frac{1}{3}}\}^2} \qquad (B.6)$$

where T is in Kelvins and P in atmospheres. $\Sigma\upsilon$ is the sum of the atomic diffusion volumes. Following the estimation method of Fuller et al.,

$$(\Sigma\upsilon)_1 = 7.07 \qquad (B.7)$$

$$(\Sigma\upsilon)_2 = 18.9 \qquad (B.8)$$

$$(\Sigma\upsilon)_3 = 2(16.5) + 4(1.98) = 40.92 \qquad (B.9)$$

$$(\Sigma\upsilon)_4 = 26.9 \qquad (B.10)$$

$$(\Sigma\upsilon)_5 = 16.5 + 4(1.98) = 26.9 \qquad (B.11)$$

$$(\Sigma\upsilon)_6 = 2(16.5) + 6(1.98) = 44.88 \qquad (B.12)$$

With $M_1 = 2.016$, $M_2 = 28.01$, $M_3 = 28.05$, $M_4 = 44.01$, $M_5 = 16.04$ and $M_6 = 30.07$, and T = 494.26 °K and $P = \frac{154.70}{14.70} = 10.53$ atms, D_{ji}'s can be determined by Eqn. (B.6) as follows

$$D_{31} = 0.1247 \text{ cm}^2/\text{s} \tag{B.13}$$

$$D_{32} = 0.0352 \text{ cm}^2/\text{s} \tag{B.14}$$

$$D_{34} = 0.0287 \text{ cm}^2/\text{s} \tag{B.15}$$

$$D_{35} = 0.0382 \text{ cm}^2/\text{s} \tag{B.16}$$

$$D_{36} = 0.0264 \text{ cm}^2/\text{s} \tag{B.17}$$

Material balance estimates the mole fraction for the six species in the gas product: $y_1 = 0.2719$, $y_2 = 0.2663$, $y_3 = 0.1108$, $y_4 = 0.1726$, $y_5 = 0.1709$ and $y_6 = 0.0075$. Substituting all known values into Eqn. (B.5) gives

$$D_{3m} = \frac{1}{\frac{0.2719}{0.1247} + \frac{0.2663}{0.0352} + \frac{0.1726}{0.0287} + \frac{0.1709}{0.0382} + \frac{0.0075}{0.0264}},$$

$$D_{3m} = 0.0487 \frac{cm^2}{s} \tag{B.18}$$

For bulk diffusion in porous solid,

$$D_{3m,eff} = \frac{D_{3m}\theta}{\tau} \tag{B.19}$$

$$= \frac{(0.0487\ cm^2/s)(0.563)}{4}$$

$$= 0.0069\ cm^2/s.$$

Assume that the diffusion process in this high-area porous catalyst is in the transition regime and that the change in number of moles in the reaction under differential conditions is small, then net effective diffusivity, D_{eff}, can be calculated by [189],

$$\frac{1}{D_{eff}} = \frac{1}{D_{3m,eff}} + \frac{1}{D_{K,eff}} \tag{B.20}$$

$$= \frac{1}{0.0069} + \frac{1}{0.0021},$$

$$D_{eff} = 0.0016 \frac{cm^2}{s}. \tag{B.21}$$

The concentration at outside particle surface, C_p, can be approximated by the concentration in the bulk gas phase, C_b, if external gradients (concentration and temperature) are negligible,

$$C_p = C_b$$

$$= \left(\frac{1\ \text{mol}}{22400\ \text{cm}^3}\right)\left(\frac{273.16\ °\text{K}}{494.26\ °\text{K}}\right)\left(\frac{10.53\ \text{atms}}{1\ \text{atm}}\right)\left(\frac{0.9237\ \text{mol}}{0.9241\ \text{mol}}\right)$$

$$= 0.0003\ \frac{\text{gm-mol}}{\text{cm}^3}. \qquad (B.22)$$

From experiment (Run # 080631029), the observed reaction rate, r, is found

$$r = 0.0638\ \frac{\text{gm-mol}}{\text{gm.cat.-hr}}$$

For 1.00 gm of catalyst bed, the static bed height = $2\frac{21}{64}$ inches = 5.91 cm, the corresponding bed volume is estimated to be 0.97 cm^3, thus,

$$r = \left(0.0638\ \frac{\text{gm-mol}}{\text{gm.cat.-hr}}\right)\left(\frac{1.00\ \text{gm.cat.}}{0.97\ \text{cm}^3\ \text{bed}}\right)\left(\frac{1\ \text{hr}}{3600\ \text{s}}\right),$$

$$\mathcal{r} = 1.83\text{x}10^{-5} \frac{\text{gm-mol}}{\text{cm}^3 \text{ bed-s}}. \tag{B.23}$$

The criterion for the absence of significant diffusion effect inside the catalyst particle is a form of the Thiele modulus and is known as Damkohler number Φ_p [15].

$$\Phi_p \equiv \frac{\mathcal{r} r_p^2}{D_{eff} C_p} < \frac{1}{|n|} \tag{B.24}$$

where r_p is the radius of particle, in cm, and n is the reaction order, and they are 0.015 cm and 0.95. Substituting the values of $\mathcal{r}$, D_{eff}, C_p from Eqns. (B.23), (B.21) and (B.22), and r_p and n into Eqn. (B.24) results in,

$$\Phi_p = \frac{(1.83\text{x}10^{-5} \frac{\text{gm-mol}}{\text{cm}^3 \text{ bed-s}})(0.015 \text{ cm})^2}{(0.0016 \frac{\text{cm}^2}{\text{s}})(0.0003 \frac{\text{gm-mol}}{\text{cm}^3})} \tag{B.25}$$

$$= 0.0099 < 1.0570$$

The criterion for insignificant diffusion inside the catalyst pellet at isothermal condition is satisfied.

Theoretical Criterion for Temperature Gradient inside Catalyst Particle

Two dimensionless groups are utilized, β and γ, in the evaluation the isothermality in the catalyst pellet, and they are defined [191],

$$\beta \text{ (heat generation function)} \equiv \frac{C_p(-\Delta H)D_{eff}}{\kappa T_p} \quad (B.26)$$

where ΔH is the enthalphy change of reaction, κ is the thermal conductivity of the porous catalyst and T_p is the temperature at outside surface of particle, and

$$\gamma \text{ (Arrhenius group)} \equiv \frac{E}{RT_p} \quad (B.27)$$

where E is the intrinsic activation energy and R is the gas constant.

For ALCOA activated alumina, $\kappa \cong 0.22 \frac{W}{m\text{-}K}$. From thermodynamic simulation (VI), $\Delta H = -6996.3$ cal for 0.8081 moles in equilibrium, hence

$$\Delta H = (-6996.3 \text{ cal})\left(\frac{1}{0.2389 \text{ cal/J}}\right)\left(\frac{1}{0.8081 \text{ mol}}\right),$$

$$\Delta H = -\ 36240.1 \ \frac{J}{mol} \qquad (B.28)$$

From kinetic model simulation (Model 6B),

$$E = \ 40090.6 \ \frac{J}{mol} \qquad (B.29)$$

Substituting values of C_p, ΔH, D_{eff}, and E from Eqns. (B.22), (B.28), (B.21), and (B.29), and using $\kappa \cong 0.22$ W/mK, $T_p \cong 494.3$ °K, and R = 8.314 J/mol-K obtains

$$\beta = \frac{(0.0003 \ \frac{gm\text{-}mol}{cm^3})(-\ 36240.1 \ \frac{J}{gm\text{-}mol})(0.0016 \ \frac{cm^2}{s})}{(0.22 \ \frac{J}{m\text{-}s\text{-}K})(\frac{1 \ m}{100 \ cm})(494.3 \ K)}$$

$$= -0.016 \qquad (B.30)$$

and

$$\gamma = \frac{40090.6 \ \frac{J}{gm\text{-}mol}}{(8.314 \ \frac{J}{gm\text{-}mol \ K})(494.3 \ K)} ,$$

$$\gamma = 9.76 \tag{B.31}$$

The criterion for the isothermality inside the catalyst pellet requires [191]:

$$\Phi_p |\beta| < \frac{1}{\gamma} \tag{B.32}$$

Plugging values of Φ_p, β and γ from Eqns. (B.25), (B.30) and (B.31) gives

$$(0.0099)|-0.016| = 0.0002 < 0.103 = \frac{1}{9.76}$$

The criterion is also satisfied, therefore isothermality should exist inside the catalyst particle.