CHAPTER III

MODELING AND SIMULATION OF AN INDUSTRIAL METHANOL
SYNTHESIS REACTOR

Consider the synthesis of methanol from synthesis gas.

$$CO \; + \; 2H_2 \; \rightleftharpoons \; CH_3OH$$

From chapter II, the equilibrium constant for the above reversible reaction is (assuming an ideal solution)

$$K \quad = \quad \frac{f_{CH_3OH}}{(f_{CO})(f_{H_2})^2}$$

Here	K	$=$	equilibrium constant $\left[atm^{-2}\right]$
and	f_i	$=$	fugacity of pure component i $[atm]$
Let	γ_i	$=$	f_i/P_i be the fugacity coefficient,
Then	K	$=$	$\dfrac{P_{CH_3OH}}{(P_{CO})(P_{H_2})^2} \cdot \dfrac{\gamma_{CH_3OH}}{(\gamma_{CO})(\gamma_{H_2})^2}$

Since $P_i = Y_i P$, we have

$$K \quad = \quad \frac{Y_{CH_3OH}}{(Y_{CO})(Y_{H_2})^2} \cdot \frac{P^1}{P^1 P^2} \cdot K_\gamma$$

The mole fraction of methanol can thus be computed from

$$Y_{CH_3OH} \quad = \quad \frac{K(Y_{CO})(Y_{H_2})^2 P^2}{K_\gamma}$$

K_γ increases with temperature but decreases with pressure while K decreases exponentially with temperature but is independent of pressure. Therefore the equilibrium composition of methanol Y_{CH_3OH} increases with pressure but decreases rapidly with temperature. This is in accordance with the basic observations of Le Chatelier's rule, as applied to a reaction that is highly exothermic and accompanied by a decrease in the total moles (3 moles of reactants $\rightarrow$ 1 mole of product). In short, high pressure and low temperature would urge the reaction toward completion.

Unfortunately all present methanol synthesis catalysts are inactive at low temperatures. This means that there exists an optimum temperature range, not too high or too low, for methanol synthesis. When methanol is synthesized in a packed bed reactor, the reaction temperature will rise gradually from the reactor inlet toward the outlet, because the reaction is exothermic. As the temperature rises, the equilibrium yield of methanol will decrease. In addition, some undersirable events such as side reactions, or excessive catalyst fouling begin to dominate. This problem can greatly be alleviated by applying cold-shot cooling between catalyst beds. The purpose of this chapter is to investigate the effect of cold-shot cooling, which is done by by-passing appropriate amounts of feed gas, on the performance of a typical four-stage industrial reactor. By trial and error, a sub-optimum cooling strategy will next be found. To do this, however, we must set up a mathematical model for the reactor. In fact, once a good model has been obtained, it can also be used as a design tool and for process simulation.

Now let's consider a adiabatic four-stage plug flow packed bed reactor, as shown in Figure 3.1. The feed stream is divided in two. One of the streams is sent directly into the reactor while the other is separated into three cooling streams and bypassed to mix directly with the outlet streams of the first three beds, respectively.

3.1 Rate of Methanol Synthesis Reaction and Its Equilibrium Constant

Consider the gaseous methanol synthesis reaction

$$CO + 2H_2 \quad \xrightarrow{\text{catalyst}} \quad CH_3OH(g)$$
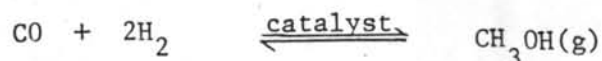
From chapter II, the rate of reaction is

$$r_c = \frac{(f_{CO})(f_{H_2})^2 - (f_{CH_3OH})/K}{(A + Bf_{CO} + Cf_{H_2} + Df_{CH_3OH})^3} \qquad \left[\frac{\text{kmol } CH_3OH}{\text{kg catalyst.hr}}\right]$$

$$(3.1)$$

Here the fugacities $f_i = y_i \gamma_i P$ and the parameters A, B, C, D are functions of temperature only. Appendix A shows the relations between A, B, C, D and temperature for an $ZnO-Cr_2O_3$ catalyst (12). The range of temperature investigated for this catalyst is $320-390^\circ C$.

The equilibrium constant K for methanol synthesis from synthesis gas is given in chapter II, namely

$$\log K = 3971 \, T^{-1} - 7.492 \log T + 1.77 \times 10^{-3}T$$
$$- 3.11 \times 10^{-8}T^2 + 9.218$$

$$(3.2)$$

Figure 3.1 Flow Diagram of the Methanol Synthesis Reactor

For simplicity, we assume that the empirical reaction rate equation (3.1) given by Natta et.al. can correctly predict the net production rate of methanol, regardless of the accompanying side reactions, such as the dehydration of methanol to dimethyl ether, etc. The rate equation is assumed valid even when there is inert gases in the system, provided their dilution effect is properly accounted for. Because of the presence of side reactions, the actual composition of the product stream, with the exception of methanol, can be slightly different from that predicted by the present simplified model. This, however, should not affect the point of investigation here, namely, the effect of cooling (bypassing) strategy on the net rate of methanol production. The same comments are applicable to the equilibrium constant K.

3.2. Mathematical Formulation of the Industrial Reactor

Figure 3.2 shows a schematic diagram of the adiabatic four-stage plug-flow packed-bed methanol synthesis reactor of interest.

The feed stream F_{ot} is divided into two parts. The first substream with a molar flow rate of $\beta_1 F_{ot}$, goes through a preheater, where its temperature is raised from T_q to T_1. Meanwhile the other substream with a molar flow rate of $(1-\beta_1) F_{ot}$, serves as a bypass cooling stream. For simplicity, we assume that each stage contains an equal amount of the same $ZnO-Cr_2O_3$ catalyst. Since the reaction is exothermic, the stream temperatue will increase from T_1 to T_1' in the first stage. To suppress the undesirable effect of high temperature on the yield of methanol, it is necessary to cool down the outlet stream by mixing with a proper fraction $\beta_2(1-\beta_1)$ of the total feed stream before sending the resultant stream into the second

F_{oa} $F_{ao1} = \beta_1 F_{oa1}$ F_{a1} F_{ao2} F_{A2} F_{ao3} F_{a3} F_{ao4} F_{a4}

F_{ob} $F_{bo1} = \beta_1 F_{ob}$ F_{b1} F_{bo2} F_{b2} F_{bo3} F_{b3} F_{bo4} F_{b4}

F_{oc} $F_{co1} = \beta_1 F_{oc}$ F_{c1} F_{co2} F_{c2} F_{co3} F_{c3} F_{co4} F_{c4}

F_{ow} $F_{wo1} = \beta_1 F_{ow}$ F_{w1} F_{wo2} F_{w2} F_{wo3} F_{w3} F_{wo4} F_{w4}

F_{on} $F_{no1} = \beta_1 F_{on}$ F_{n1} F_{no2} F_{n2} F_{no3} F_{n3} F_{no4} F_{n4}

F_{ot} $F_{to1} = \beta_t F_{ot}$ F_{t1} F_{to2} F_{t2} F_{to3} F_{t3} F_{to4} F_{t4}
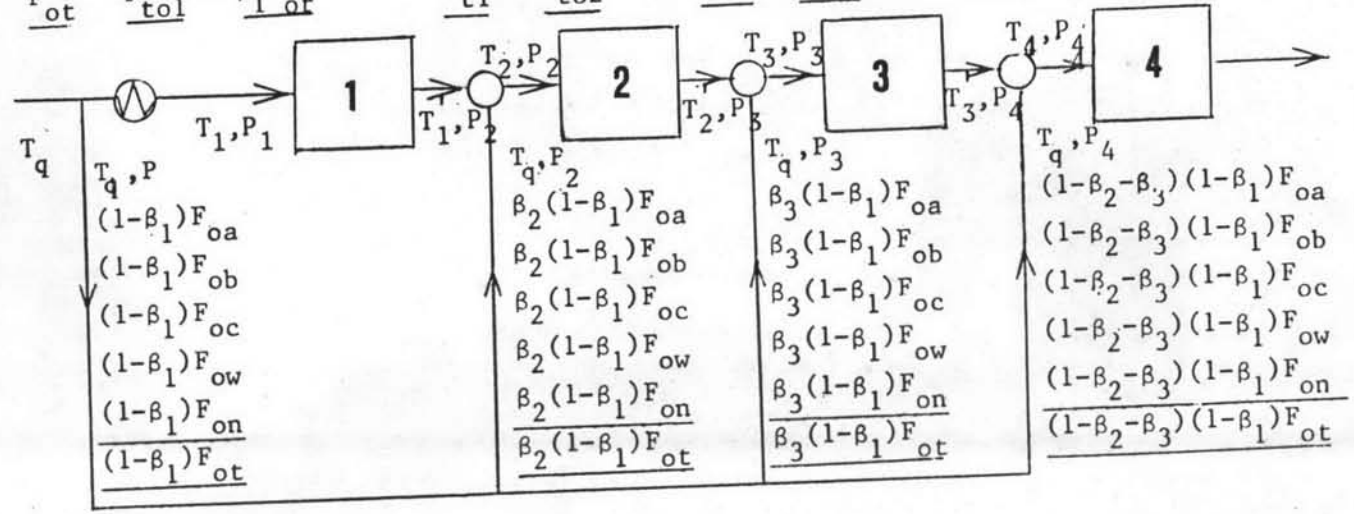
T_q

T_q,P
$(1-\beta_1)F_{oa}$
$(1-\beta_1)F_{ob}$
$(1-\beta_1)F_{oc}$
$(1-\beta_1)F_{ow}$
$(1-\beta_1)F_{on}$
$(1-\beta_1)F_{ot}$

T_q,P_2
$\beta_2(1-\beta_1)F_{oa}$
$\beta_2(1-\beta_1)F_{ob}$
$\beta_2(1-\beta_1)F_{oc}$
$\beta_2(1-\beta_1)F_{ow}$
$\beta_2(1-\beta_1)F_{on}$
$\beta_2(1-\beta_1)F_{ot}$

T_q,P_3
$\beta_3(1-\beta_1)F_{oa}$
$\beta_3(1-\beta_1)F_{ob}$
$\beta_3(1-\beta_1)F_{oc}$
$\beta_3(1-\beta_1)F_{ow}$
$\beta_3(1-\beta_1)F_{on}$
$\beta_3(1-\beta_1)F_{ot}$

T_q,P_4
$(1-\beta_2-\beta_3)(1-\beta_1)F_{oa}$
$(1-\beta_2-\beta_3)(1-\beta_1)F_{ob}$
$(1-\beta_2-\beta_3)(1-\beta_1)F_{oc}$
$(1-\beta_2-\beta_3)(1-\beta_1)F_{ow}$
$(1-\beta_2-\beta_3)(1-\beta_1)F_{on}$
$(1-\beta_2-\beta_3)(1-\beta_1)F_{ot}$

T_1,P_1 T_1,P_2 T_2,P_2 T_2,P_3 T_3,P_3 T_3,P_4 T_4,P_4

Boxes: 1   2   3   4

Figure. 3.2 Schematic Diagram of the Reactor System

stage. In this way, the temperature of the entering stream to the second stage becomes T_2. The stream then emerges from the second stage at temperature T_2', and again is cooled to T_3 by direct mixing with a fraction $\beta_3(1-\beta_1)$ of the total feed stream. Similarly, the stream that emerges from the third stage at T_3' is cooled to T_4 by direct mixing with $\beta_4(1-\beta_1)$ of F_{ot} before entering the fourth stage. Obviously, the choice of $\beta_1, \beta_2, \beta_3$ and β_4 $(\beta_4 = 1-\beta_2-\beta_3)$ can lower or increase the overall production rate (per pass) of methanol in the whole reactor.

Differential equations for the steady-state material, energy, and momentum balances, as applied to the synthesis reactor shown in Figure 3.2 will now be derived. The following basic assumptions are made.

    1. The whole system is in a steady state.

    2. The flow inside each stage of the reactor is assumed to be plug (piston) flow.

    3. The whole system is adiabatic.

    4. Side reactions to methanol synthesis, such as formation of CO_2, methanation of CO, etc, can be ignored, as long as the correct rate of methanol synthesis can be predicted.

    3.2.1 Material Balance of Component i over ΔZ of Any Reactor Stage of Interest

Z Z+ΔZ
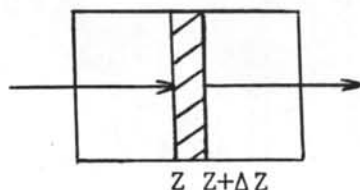
Since

$$F_i\Big|_Z - F_i\Big|_{Z+\Delta Z} + r_i A_r \Delta Z \rho_s (1-\varepsilon) = 0$$

we have

$$\frac{dF_i}{dZ} = r_i A_r \rho_s (1-\varepsilon) \qquad \text{--------(3.3)}$$

The molar flow rates at Z in the reactor are :

$$F_a = F_{ao} - F_{ao}(X_a) = F_{ao}(1-X_a) \text{--------(3.3)}$$

$$F_b = F_{bo} - 2F_{ao}(X_a) = F_{ao}(\theta_b - 2X_a) \text{-------(3.4)}$$

$$F_c = F_{co} + F_{ao}(X_a) = F_{ao}(\theta_c + X_a) \text{--------(3.5)}$$

$$F_w = F_{wo} \qquad \text{--------(3.6)}$$

$$F_n = F_{no} \qquad \text{--------(3.7)}$$

$$F_t = F_a + F_b + F_c + F_w + F_n \quad \text{--------(3.8)}$$

Here $\quad \theta_b = F_{bo}/F_{ao} \;,\; \theta_c = F_{co}/F_{ao}$

and $\quad F_{io}$ (kmol/hr) is the inlet molar flow rate of component i into each stage of the reactor.

Specifically, the methanol balance is

$$\frac{d}{dZ} F_{ao}(\theta_c + X_a) = r_c A_r \rho_s (1-\varepsilon)$$

or

$$\frac{dX_a}{dZ} = \frac{r_c A_r \rho_s (1-\varepsilon)}{F_{ao}} \qquad \text{--------(3.9)}$$

where

r_c = rate of methanol synthesis, kmol/kg catalyst.hr.

A_r = cross-sectional area of catalyst bed, m^2

ε = voidage of catalyst bed

ρ_s = bulk density of catalyst pellets, kg/m^3-pellet

X_a = conversion of incoming CO to CH_3OH

Z = distance in catalyst bed, m

The subscript a,b,c,w and n for the components are as follows:, a = CO; b = H_2; c = CH_3OH; w = H_2O; n = N_2. The rate of methanol formation from equation (3.1) is

$$r_c = \frac{(f_{CO})(f_{H_2})^2 - (f_{CH_3OH})/K}{(A + B\,f_{CO} + C\,f_{H_2} + D\,f_{CH_3OH})^3}$$

The following curve-fitting equations have been obtained for A,B,C,D (See Appendix A)

$A = -2248.3699 + 399.3158\ \ln t$ $\left[atm.(kg\ catalyst.hr/kmol)^{\frac{1}{3}} \right]$

$B = 888.931\ exp\ (0.016736t)$ $\left[(kg\ catalyst.hr/kmol)^{\frac{1}{3}} \right]$

$C = 34.3665 - 0.13745\ t - 2.31 \times 10^{-4} t^2 + 1.61 \times 10^{-6} t^3$
     $- 1.77 \times 10^{-9} t^4$ $\left[(kg\ catalyst.hr/kmol)^{\frac{1}{3}} \right]$

$D = 41612.48\ exp(0.02326t)$ $\left[(kg\ catalyst.hr/kmol)^{\frac{1}{3}} \right]$

Here   t = reaction temperature $\left[{}^{\circ}C \right]$

The fugacity of component i is given by

$$f_i = Y_i P' \gamma_i \qquad\qquad \left[atm \right]$$

Where Y_i is the mole fraction of component i, P' is the total pressure of the system, atm, and γ_i is the fugacity coefficient, which can be estimated with the aid of Hougen and Watson (13) . Furthermore, the equilibrium constant K, atm^{-2}, is expressed as

$$\log K = 3971\ T^{-1} - 7.492 \log T + 1.77 \times 10^{-3} T$$
$$-3.11 \times 10^{-8}\ T^2 + 9.218$$

Where T is the absolute reaction temperature, ^{o}K

Note that $r_a = -r_c$, $r_b = -2r_c$, and $r_w = r_n = 0$

3.2.2 Energy Balance over ΔZ of Any Reactor Stage of Interest

$$\Sigma F_i C_{pi}(T-T_o)\big|_Z -\Sigma F_i C_{pi}(T-T_o)\big|_{Z+\Delta Z} + r_c(dv)\rho_s(1-\epsilon)(-\Delta H_r) = 0$$

$$\Sigma F_i C_{pi}(T-T_o)\big|_Z -\Sigma F_i C_{pi}(T-T_o)\big|_{Z+\Delta Z} + F_{ao}(dX_a)(-\Delta H_r) = 0$$

$$\Sigma F_i C_{pi}\frac{dT}{dZ} = F_{ao}\frac{dX_a}{dZ}(-\Delta H_r)$$

$$\frac{dT}{dZ} = \frac{F_{ao}(-\Delta H_r)}{\Sigma F_i C_{pi}} \cdot \frac{dX_a}{dZ} \quad \text{-------(3.10)}$$

Generally the specific heat C_{pi} is a function of temperature and pressure (14). Specifically, at any T and P,

$$C_{pi} = C_{pi}^o + \Delta C_{pi} \quad \text{-------(3.11)}$$

Where the ideal-gas state (zero-pressure) specific heat C_{pi}^o is function of the temperature T only. In this study, we use the specific heat at 1 atm for C_{pi}^o , as follows :

$$C_{pa}^{'o} = 7.373 - 0.307 \times 10^{-2}T + 6.662 \times 10^{-6}T^2 - 3.037 \times 10^{-9}T^3 \left[kcal/kmol \,^oK \right]$$

$$C_{pb}^{'o} = 6.483 + 2.215 \times 10^{-3}T - 3.298 \times 10^{-6}T^2 + 1.826 \times 10^{-9}T^3$$

$$C_{pc}^{'o} = 5.052 + 1.694 \times 10^{-2}T + 6.179 \times 10^{-6}T^2 - 6.811 \times 10^{-9}T^3$$

$$C_{pw}^{'o} = 7.701 + 4.595 \times 10^{-4}T + 2.521 \times 10^{-6}T^2 - 0.859 \times 10^{-9}T^3$$

$$C_{pn}^{'o} = 7.440 - 0.324 \times 10^{-2}T + 6.400 \times 10^{-6}T^2 - 2.790 \times 10^{-9}T^3$$

$$C_p^o = C_p^{'o} . 4.184 \text{ kJ/kcal} \qquad \left[kJ/kmol.\,^oK \right]$$

The correction factor ΔC_{pi} takes account of the effect of pressure on the specific heat.

ΔC_{pi} can be calculated from

$$\Delta C_{pi} = \frac{\partial}{\partial T} \left[(H_i - H_i^o) \right]_P \qquad \text{--------(3.12)}$$

The term $(H_i - H_i^o)$ is the "departure function" of enthalpy, obtainable from equation (3.13)

$$H_i - H_i^o = (A_i - A_i^o) + T(S_i - S_i^o) + RT(Z_i - 1) \qquad \text{--------(3.13)}$$

For a mixture of constant temperature and composition, the variation in the Helmholtz energy with molar volume V_i is

$$dA_i = -PdV_i$$

Integrating at constant temperature and composition from the reference volume V_i^o (where $A_i = A_i^o$) to the system volume V_i gives

$$A_i - A_i^o = - \int_{V_i^o}^{V_i} PdV_i$$

Next we break the integral into two parts, namely

$$A_i - A_i^o = - \int_{\infty}^{V_i} PdV_i - \int_{V_i^o}^{\infty} PdV_i$$

$$-------(3.14)$$

The first integral involves real-gas properties, that is, $P = f(V_i)$ at constant temperature T, while the second is written for an ideal gas and can be integrated immediately. Before doing so, however, to avoid the difficulty introduced by the infinity limit, we add and subtract $\int_{\infty}^{V_i} (RT/V_i)dV_i$ from the right-hand side. Then

$$A_i - A_i^o = -\int_{\infty}^{V_i} \left(P - \frac{RT}{V_i} \right) dV_i - RT \ln\frac{V_i}{V_i^o}$$

$$-------(3.15)$$

Using the Redlich-Kwong equation of state

$$Z_i = \frac{PV_i}{RT} = \frac{V_i}{V_i - b_i} - \frac{\Omega_x}{\Omega_y} \frac{b_i F_{mi}}{(V_i + b_i)}$$

$$-------(3.16)$$

Equation (3.15) becomes

$$A_i - A_i^O = -\int_{\infty}^{V_i}\left[\frac{RT}{V_i - b_i} - \frac{RT}{V_i} - \frac{\Omega_x}{\Omega_y}\frac{RTb_i F_{mi}}{V_i(V_i + b_i)}\right]dV_i - RT\ln\frac{V_i}{V_i^O}$$

$$= -\left[RT\ln\frac{(V_i - b_i)}{V_i} + \frac{\Omega_x}{\Omega_y}RT\,F_{mi}\ln\frac{(V_i + b_i)}{V_i}\right]$$

$$-RT\ln\frac{V_i}{V_i^O}$$

$$= -RT\ln\frac{(V_i - b_i)}{V_i} - \frac{\Omega_x}{\Omega_y}RT\,F_{mi}\ln\frac{(V_i + b_i)}{V_i} - RT\ln\frac{V_i}{V_i^O}$$

Now

$$S_i - S_i^O = -\left[\frac{\partial(A_i - A_i^O)}{\partial T}\right]_{V_i}$$

$$= -\left[-R\ln\frac{(V_i - b_i)}{V_i} - \frac{\Omega_x}{\Omega_y}R(1 - \theta_i)\ln\frac{(V_i + b_i)}{V_i}\right.$$

$$\left. - R\ln\frac{V_i}{V_i^O}\right]$$

Therefore,

$$H_i - H_i^O = -\frac{\Omega_x}{\Omega_y}RT_{ci}\,\theta_i\ln\frac{(V_i + b_i)}{V_i} + RT(Z_i - 1)$$

and

$$\frac{\partial}{\partial T}\left[(H_i - H_i^O)\right]_P = \frac{\Omega_x}{\Omega_y}\frac{Rb_i\,\theta_i\,T_{ci}}{(v_i + b_i)V_i}\frac{\partial V_i}{\partial T} + P\frac{\partial V_i}{\partial T} - R$$

Thus equation (3.11) becomes

$$C_{pi} = C_{pi}^O + \frac{\Omega_x}{\Omega_y}\frac{Rb_i\,\theta_i\,T_{ci}}{(V_i + b_i)V_i}\frac{\partial V_i}{\partial T} + P\frac{\partial V_i}{\partial T} - R$$

$$--------(3.17)$$

The heat of reaction, $-\Delta H_r$ is a function of temperature and pressure, as follows

$$\Delta H_r = \Delta H_o + \int_{T_o}^{T} \Delta C_p^o \, dT + \int_{P_o}^{P} (\Delta V) dP - T \int_{P_o}^{P} \left(\frac{\partial \Delta V}{\partial T}\right)_P dP$$

$$-------(3.18)$$

Where ΔH_o is the standard heat of reaction at atmospheric pressure and reference temperature (25^oC), kJ/kmol-CO; ΔV is the change in molar volume of the products and reactants of the methanol synthesis reaction, i.e.

$$\Delta V = V_c - V_a - 2V_b \qquad \left[m^3/\text{kmol-CH}_3\text{OH} \right]$$

V_i is obtained from solving the Redlich-Kwong equation of state, Equation (3.16), which is rewritten as

$$V_i^3 - \frac{RT}{P} V_i^2 - \left(\frac{\Omega_x}{\Omega_y} b_i^2 - \frac{\Omega_x}{\Omega_y} \frac{b_i F_{mi} RT}{P} \right) V_i - \left(\frac{RTb_i}{P} + \frac{\Omega_x}{\Omega_y} \frac{b_i^2 F_{mi} RT}{P} \right) = 0$$

Furthermore,

$$\frac{\partial V_i}{\partial T} = \frac{RV_i/P(V_i - b_i) - \Omega_x b_i R(1-\theta_i)/\Omega_y (V_i + b_i) P}{1 - RT/P(V_i - b_i) + RTV/P(V_i - b_i)^2 - \Omega_x b_i RTF_{mi}/\Omega_y (V_i + b_i)^2 P}$$

Then we obtain

$$\frac{\partial \Delta V_i}{\partial T} = \frac{\partial V_c}{\partial T} - \frac{\partial V_a}{\partial T} - 2 \frac{\partial V_b}{\partial T} \qquad \left[m^3/\text{kmol.}^o\text{K} \right]$$

Where

R = gas constant , 8.314 kJ/kmol^{o}K

V_i = molar volume of component i, m^3/kmol

Ω_x = $[(9)(2^{1/3} - 1)]^{-1}$ = 0.4274802327 .....

Ω_y = $\dfrac{2^{1/3} - 1}{3}$ = 0.086640350 ....

b_i = $\dfrac{\Omega_y R T_{ci}}{P_{ci}}$, m^3/kmol

b = $\sum_i Y_i b_i$, m^3/kmol

F_m = $\sum_i Y_i F_{mi}$

F_{mi} = $1 + \theta_i (T_{ri}^{-1} - 1)$

θ_i = $1.57 + 1.62\,\omega_i$

ω_i = Pitzer's acentric factor

T_{ri} = T/T_{ci}

T_{ci}, P_{ci} are the critical temperature and pressure respectivety, and ω_i is the Pitzer's acentric factor, the values of which are shown below.

T_{ca} = 132.9^{o}K $\quad$ P_{ca} = 34.937 x 10^2 kN/m^2 $\quad$ ω_a = 0.049

T_{cb} = 33.2^{o}K $\quad$ P_{cb} = 12.97 x 10^2 kN/m^2 $\quad$ ω_b = -0.22

T_{cc} = 512.6^{o}K $\quad$ P_{cc} = 79.721x 10^2 kN/m^2 $\quad$ ω_c = 0.559

T_{cw} = 647.3^{o}K $\quad$ P_{cw} = 22.129 x 10^3 kN/m^2 $\quad$ ω_w = 0.344

T_{cn} = 126.2^{o}K $\quad$ P_{cn} = 33.944 x 10^2 kN/m^2 $\quad$ ω_n = 0.040

3.2.3 Pressure Drop over ΔZ in Any Reactor Bed of Interest

Resistance to the gas flow is measured by the pressure drop across the bed. The pressure drop may be estimated by the well-known Ergan equation (16).

$$\frac{\Delta P}{\Delta Z} = \frac{150 \mu \, V_o (1-\epsilon)^2}{D_P^2 \, \epsilon^3} + \frac{1.75 \, \rho \, V_o^2 (1-\epsilon)}{D_P \, \epsilon^3} \qquad \text{--------(3.19)}$$

ΔP = pressure drop $\left[N/m^2 \right]$

μ = viscosity of fluid $\left[kg/m.s \right]$

ΔZ = length of bed $\left[m \right]$

V_o = superficial fluid velocity based on empty-reactor cross section $\left[m/s \right]$

D_P = effective diameter of particle $\left[m \right]$ as defined by

$D_P = \dfrac{6V_{pat.}}{A_P} = \dfrac{6 \, \pi r^2 L}{2 \, \pi rL + 2\pi r^2}$ (cylinder case)

A_P = surface area of particle $\left[m^2 \right]$

$V_{pat.}$ = volume of particle $\left[m^3 \right]$

ρ = density of fluid $\left[kg/m^3 \right]$

The viscosity of fluid , μ is a function of temperature and pressure. The Theory of Chapman-Enskag (15) can be used to determine the viscosity of a low-pressure multicomponent gas mixture.

The expression is relatively complicated and consists of the ratio of two determinants, which contain elements involving mole fractions, molecular weights, pure-component viscosities , temperature, and various collision integrals. The solution can be approximated in a series as

$$\mu^o = \frac{\sum\limits_{i}^{n} Y_i \mu_i^o}{\sum\limits_{j}^{n} Y_i \Phi_{ij}}$$

The pure-component viscosities, μ_i^o is determined by curve-fitting (Appendix B) as :

$$\mu_a'^o = 0.02125 - 3.0 \times 10^{-5} t + 3.38 \times 10^{-7} t^2 - 6.35 \times 10^{-10} t^3 + 3.96 \times 10^{-13} t^4 \quad [\text{cP}]$$

$$\mu_b'^o = 7.48 \times 10^{-3} + 4.05 \times 10^{-5} t - 1.27 \times 10^{-7} t^2 + 2.62 \times 10^{-10} t^3 - 1.87 \times 10^{-13} t^4$$

$$\mu_c'^o = 8.47 \times 10^{-3} + 4.22 \times 10^{-5} t - 4.89 \times 10^{-8} t^2 + 1.09 \times 10^{-10} t^3 - 8.33 \times 10^{-14} t^4$$

$$\mu_w'^o = 8.67 \times 10^{-3} + 3.98 \times 10^{-5} t - 1.93 \times 10^{-8} t^2 + 5.09 \times 10^{-11} t^3 - 4.16 \times 10^{-14} t^4$$

$$\mu_n'^o = 0.01650 - 2.16 \times 10^{-5} t + 3.3 \times 10^{-7} t^2 - 7.00 \times 10^{-10} t^3 + 5.0 \times 10^{-13} t^4$$

$$\mu^o = \mu'^o \cdot 10^4 \frac{\mu P}{cP} \quad , \quad [\mu P]$$

To estimate the parameters Φ_{ij} , we use Wike's approximation (15).

$$\Phi_{ij} = \frac{(1 + (\mu_i^o/\mu_j^o)^{\frac{1}{2}} (M_i/M_i)^{\frac{1}{4}})^2}{(8(1 + M_i/M_j))^{\frac{1}{2}}}$$

Where

M_i , M_j = pure component molecular weight

Dean and Stiel has suggested a method to find the viscosities of dense-gas mixtures (15) which reads

$$(\mu - \mu^o)\xi \;=\; (1.08)\left[\exp 1.439\,\rho_{rm} - \exp(-1.111\rho_{rm}^{1.858})\right]$$

Where

$$\mu \;=\; \text{high pressure mixture viscosity} \quad [\mu P]$$

$$\mu^o \;=\; \text{low pressure mixture viscosity} \quad [\mu P]$$

$$\rho_{rm} \;=\; \text{pseudoreduced mixture density}, \quad \rho_m/\rho_{cm}$$

$$\rho_m \;=\; \text{mixture density} \quad \left[kmol/m^3\right]$$

$$\rho_{cm} \;=\; \text{pseudocritical mixture density} \quad \left[kmol/m^3\right],$$

$$\qquad\qquad P_{cm}/Z_{cm}RT_{cm}$$

$$\xi \;=\; T_{cm}^{\frac{1}{6}}/M_m^{\frac{1}{2}}\,P_{cm}^{\frac{2}{3}}$$

The mixture molecular weight M_m is a mole-fraction average. The pseudocritical mixture parameters Z_{cm}, T_{cm}, and P_{cm} must be calculated using an appropriate pseudocritical-constant rule. Dean and Stiel recomments the modified Prausnitz and Gunn rules :

$$T_{cm} \;=\; \sum_i Y_i T_{ci}$$

$$Z_{cm} \;=\; \sum_i Y_i Z_{ci}$$

$$V_{cm} \;=\; \sum_i Y_i V_{ci}$$

$$P_{cm} \;=\; \frac{Z_{cm}RT_{cm}}{V_{cm}}$$

These pseudocritical values are then used to calculate ρ_{cm} and ξ.

Next we consider the quench point at the end of each bed (except the last).

3.2.4 Material Balance at the Quench Point

When the bypassed gas (molar flow rate, F_q) is used to quench the outlet gas of a catalyst, the resulting molar flow rates of the quenched gases into the next bed become :

$$F_{ao} = F_a + F_{aq}$$

$$F_{bo} = F_b + F_{bq}$$

$$F_{co} = F_c + F_{cq} \qquad\qquad ----- (3.20)$$

$$F_{wo} = F_w + F_{wq}$$

$$F_{no} = F_n + F_{nq}$$

The molar flow rate of component i, F_{io}, into the first bed of reactor is given by

$$F_{ao} = \beta_1 (F_{oa})$$

$$F_{bo} = \beta_1 (F_{ob})$$

$$F_{co} = \beta_1 (F_{oc})$$

$$F_{wo} = \beta_1 (F_{ow})$$

$$F_{no} = \beta_1 (F_{on})$$

Where β_1 = mole fraction of total feed gas sent directly into the first stage. Thus the total molar flow rate of bypassed gas is $(1-\beta_1)F_{oi}$.

The molar flow rate of bypassed gas used to quench the effuent of the first stage is

$$F_{aq} = \beta_2(1-\beta_1)F_{oa}$$

$$F_{bq} = \beta_2(1-\beta_1)F_{ob}$$

$$F_{cq} = \beta_2(1-\beta_1)F_{oc}$$

$$F_{wq} = \beta_2(1-\beta_1)F_{ow}$$

$$F_{nq} = \beta_2(1-\beta_1)F_{on}$$

Similarly, the molar flow rate of bypassed gas used to quench the effuents of the second and third stages are as shown below.

$$F_{aq} = \beta_3(1-\beta_1)F_{oa}$$

$$F_{bq} = \beta_3(1-\beta_1)F_{ob}$$

$$F_{cq} = \beta_3(1-\beta_1)F_{oc}$$

$$F_{wq} = \beta_3(1-\beta_1)F_{ow}$$

$$F_{nq} = \beta_3(1-\beta_1)F_{on}$$

$$F_{aq} = (1-\beta_2-\beta_3)(1-\beta_1)F_{oa}$$

$$F_{bq} = (1-\beta_2-\beta_3)(1-\beta_1)F_{ob}$$

$$F_{cq} = (1-\beta_2-\beta_3)(1-\beta_1)F_{oc}$$

$$F_{wq} = (1-\beta_2-\beta_3)(1-\beta_1)F_{ow}$$

$$F_{nq} = (1-\beta_2-\beta_3)(1-\beta_1)F_{on}$$

Where

β_2 = mole fraction of total bypassed gas used to quench the effluent of the first stage

β_3 = mole fraction of total bypassed gas used to quench the effluent of the second stage

3.2.5 Energy Balance at the Quench Point

$$\Sigma F_i \int_{T_o}^{T} C_{pi} dT + \Sigma F_{iq} \int_{T_o}^{T_q} C_{pi} dT = (\Sigma F_i + \Sigma F_i) C_{pi} (\frac{T+T_q}{2}, P)(T_m - T_o)$$

$$T_m = \frac{(\Sigma F_i \int_{T_o}^{T} C_{pi} dT + \Sigma F_{iq} \int_{T_o}^{T_q} C_{pi} dT)}{(\Sigma F_i + \Sigma F_{iq}) C_{pi} \frac{(T + T_q}{2}, P)} + T_o \quad \text{-------(3.21)}$$

Where T_q = temperature of bypassed gas $[^oK]$

T_o = a reference temperature, T_q $[^oK]$

T_m = temperature of quenched gas $[^oK]$

$C_{pi}(\frac{T+T_q}{2}, P)$ = molar specific heat at the average temperature and total pressure

It is assumed that the pressure of the quench gas is adjusted to the value of the effluent gas from the stage of interest.

The material and energy balances, equations (3.9),(3,10), can be integrated to give the local composition and temperatue with in a catalyst bed, provided its inlet composition and temperature are known. In this work, the Euler method is used to integrate equations (3.9),(3.10), numerically.

The heat of reaction, $-\Delta H_r$ is obtained by solving equation (3.18), and the integral terms are evaluated using the trapezoidal rule. Pressure drop along the bed is obtained using equation (3.19). In this manner, we are able to obtain the local composition, temperature and pressure in each stage (catalyst bed), as well as their outlet values. The composition and temperature of the resulting

gas from quenching the effluent with some of the total bypassed
gas can be estimated from equation (3.20) and equation (3.21).

Figure 3.3 is a block diagram of the computer program deve-
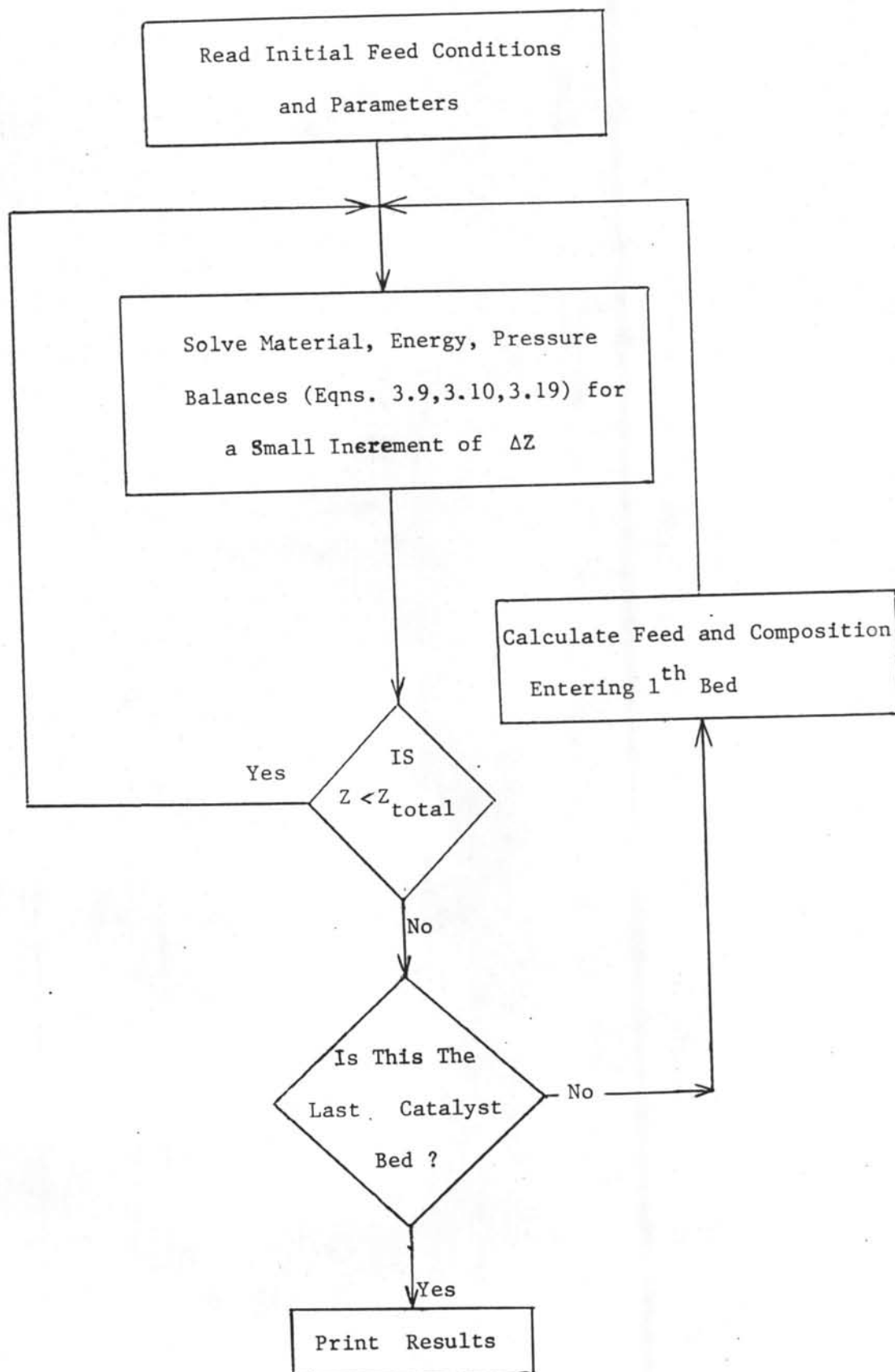loped to simulate the present adiabatic four-stage plug-flow
packed bed reactor.

Figure 3.3 Block Diagram of Computer Simulation Program