CHAPTER 5

DEVELOPMENT OF MATHEMATICAL MODEL FOR
DEVOLATILIZATION PHASE

5.1 Introduction

Devolatilization is the second phase of the droplet dynamics in the recovery boiler. Though both drying and devolatilization are concurrent processes (Jarvinen et al., 2002b), these processes are assumed as exclusive processes for simplifying the modeling. Devolatilization is an endothermic reaction. The droplet, while moving down in the recovery furnace, receives heat from hot gases through convection and radiation from the char bed. After attaining the pyrolysis temperature, the droplet starts losing its mass in the form of volatiles due to de-polymerization (Biagini et al., 2009) and this process is called devolatilization. The total heat received as convective and radiative heat by the droplet in an incremental time period is utilized as heat of devolatilization for releasing volatiles and raising the temperature of the droplet. The release of volatiles depends on the organic content of the black liquor, temperature of the furnace and heat transfer to the particle. In the current chapter it is sought to model the droplet dynamics during the devolatilization phase. The kinetics of devolatilization, which helps in estimating the release of volatiles from the droplet at any temperature for a given time interval, was discussed in the previous chapter (Chapter 4).

While the droplets move down after being sprayed in the recovery furnace, some of the droplets are carried over due to the drag force by the upward moving hot gases. It is attempted to capture

a) All the parameters which hinder the particle to reach the char bed and dominate the action of carryover phenomena

b) Particles reaching the char bed in wet condition.
5.2 Transition pyrolysis

Transition pyrolysis is a transition or an intermediate phase which falls in between drying and pyrolysis. In this phase, temperature of the droplet rises till the droplet attains the pyrolysis temperature.

The total heat received by the droplet in an incremental time period as convective and radiative heat is utilized as sensible heat to raise the temperature of the droplet till the droplet attains the pyrolysis temperature. It is evident from the experimental data (Chapter 4) that devolatilization is negligible till the particle attains ~300° C. Hence all the heat absorbed by the droplet is utilized exclusively for raising the temperature till the droplet attains 300°C.

When the black liquor droplet moves down in the hot ambience of furnace after completing the drying phase, the heat that is transferred to the particle in the form of convective heat transfer from the surrounding hot gases and radiation heat transfer from the char bed increases the temperature till the droplet attains the pyrolysis temperature. In this section, equations are given for estimating the quantum of heat that is transferred to the particle both by convective & radiation heat transfer, rise in sensible heat content which help in estimating the particle temperature.

5.2.1 List of assumptions used (Adams et al., 1988)

a) Drying is completed before onset of this phenomenon
b) No devolatilization occurs during this process and there is no change in mass of the droplet.
c) Droplet is assumed as spherical in shape (Jarvinen, 2002b; Teng-Ip, 2005).
d) Temperature profile (Engblom, 2012b) of the gases is assumed as given in the Table 3.1.
e) The maximum travel distance of the droplet is assumed as 5.5 m (Macek, 1999). This is the distance between the injection point and the char bed.
f) No swelling takes place.

Overall heat balance can be written as

\[ Q_{in} - Q_{out} = Q_{acc} \] (5.1)

Where
\[ Q_{\text{out}} = 0 \]  \hspace{1cm} (5.2)
\[ Q_{\text{acc}} = Q_{\text{sen}} \]  \hspace{1cm} (5.3)

And
\[ Q_{\text{sen}} = W_p C_p^{BL} T_{pC} \]  \hspace{1cm} (5.4)

Equation (5.1) can be re written as
\[ Q_{\text{in}} = W_p C_p^{BL} T_{pC} \]  \hspace{1cm} (5.5)

Equation 5.5 can be expressed for incremental time period
\[ Q_{\text{in}}^{j+1} - Q_{\text{in}}^j = W_p C_p^{BL} (T_{pC}^{j+1} - T_{pC}^j) \]  \hspace{1cm} (5.6)

The new particle temperature can be estimated from the expression
\[ T_{pC}^{j+1} = \frac{Q_{\text{in}}^{j+1} - Q_{\text{in}}^j}{W_p C_p^{BL}} + T_{pC}^j \]  \hspace{1cm} (5.7)

The heat \((Q_{\text{in}})\) transferred to a spherical drop by convection & radiation are estimated as explained in chapter 3.
\[ Q_{\text{in}} = Q_{\text{conv}} + Q_{\text{rad}} \]

The model equations (3.21) for the droplet velocity in the boiler and its discretized form (3.24) as discussed in chapter 3 are
\[ \frac{du_p}{dt} = \frac{(\rho_p - \rho_g)}{\rho_p} g - \frac{3C_p \rho_g}{4D_p \rho_p} (u_g + u_p)^2 \]  \hspace{1cm} (5.8)
\[ u_p^{j+1} = u_p^j + \left[ \frac{(\rho_p - \rho_g)}{\rho_p} g - \frac{3C_p \rho_g}{4D_p \rho_p} (u_g^j + u_p^j)^2 \right] \Delta t \]  \hspace{1cm} (5.9)

The model equation for the droplet travel distance (Eq. 3.47) as discussed in chapter 3 is
\[ T_p^j = T_p^{j-1} + u_p^j (t^j - t^{j-1}) \]  \hspace{1cm} (5.10)

The simultaneous solution of equations 5.7, 5.9, 5.10 give the new values of particle temperature, particle velocity and particle travel distance at the end of the incremental time period and these values are used as initial values for solving the next set of equations till the particle attains 300°C or reaches char bed.
5.3 Pyrolysis

After attaining the pyrolysis temperature, rise in heat content with in the droplet releases some volatiles, loses some heat content as heat of devolatilization and the remaining heat is utilized as sensible heat of the droplet there by increasing the temperature of the droplet. In this section, equations are given for estimating the quantum of heat transferred to the particle both by convective & radiation heat transfer, rise in heat content, loss of heat in the form of heat of devolatilization and there by estimating the mass loss which helps in estimating the residual droplet weight.

5.3.1 List of assumptions used (Adams et al., 1988)

a. Droplet is assumed as spherical in shape (Jarvinen, 2002b; Teng-Ip, 2005)
c. Swelling factor is assumed as constant for the devolatilization phase.
d. During the iteration interval, the droplet is assumed isothermal while estimating mass loss.
e. Temperature profile (Engblom, 2012b) of the gases is assumed as given in Table 3.1.
f. Drying, Devolatilization & char combustion are assumed as exclusive phenomena (Jarvinen, 2002b).
g. Thermal conductivity and density of the air are taken for furnace gases.

5.4 Swelling phenomena in Pyrolysis

Swelling (Jarvinen et al., 2003a) is one of the important characteristics of black liquor. The droplet normally, after attaining pyrolysis temperatures, starts evolving volatiles and in this process particle swells. The ratio of the final diameter of the droplet and initial diameter of the droplet is expressed as swelling factor or index.

5.5 Simultaneous Heat and Mass Transfer

The overall heat balance during pyrolysis of a droplet moving in hot ambience can be written as

$$Q_{in} - Q_{out} = Q_{sen}$$  \hspace{1cm} (5.11)

Where
\[ Q_{\text{in}} = Q_{\text{conv}} + Q_{\text{rad}} \]
\[ Q_{\text{out}} = Q_{\text{devol}} \]
\[ Q_{\text{sen}} = W_p C_P^{BL} T_p C \]

The heat \((Q_{\text{conv}})\) transferred to a spherical drop by convection (McCabe, 1985) is
\[ Q_{\text{conv}} = h A_p \Delta T \quad (5.12) \]

The convective heat transfer coefficient can be determined from the Nusselt number (Macek, 1999) and it is estimated by using a correlation as a function of the dimensionless Grashof number \((Gr)\) and particle Reynolds number \((Re_p)\).
\[ Nu = 2 + 0.39Gr^{0.25} + 0.37Re_p^{0.6} \quad (5.13) \]

The heat \((Q_{\text{rad}})\) that is to be transferred to a spherical drop by radiation (Grace et al., 1998c) from the char bed can be estimated by the expression (Eq. 3.30)
\[ Q_{\text{rad}} = A \sigma (\alpha (T_{cbK}) T_{cbK}^4 - \varepsilon (T_{pK}) T_{pK}^4) \quad (5.14) \]

The volatiles removed in unit time is the ratio of available heat for devolatilization in unit time \((Q_{\text{devol}})\) and heat of devolatilization \((h_{\text{devol}})\) per kg of volatiles and it can be expressed as
\[ \frac{d(BL_{\text{wt}})}{dt} = \frac{Q_{\text{devol}}}{h_{\text{devol}}} \quad (5.15) \]

Discretizing the Eq. 5.15 for obtaining the mass loss in incremental time period
\[ BL_{\text{wt}}^{j+1} - BL_{\text{wt}}^j = \frac{Q_{\text{devol}}^{j+1} - Q_{\text{devol}}^j}{h_{\text{devol}}} \quad (5.16) \]

The mass loss in incremental time period is estimated by Eq. 4.1.

The heat consumed in this process is estimated by the expression Eq. 5.17 with the estimated mass loss in incremental time period.
\[ delQ_{\text{devol}} = (BL_{\text{wt}}^{j+1} - BL_{\text{wt}}^j) \times h_{\text{devol}} \quad (5.17) \]

Heat received \((Q_{\text{in}})\) in incremental time period \((\Delta t)\) can be written as
\[ delQ_{\text{in}} = Q_{\text{in}} \times \Delta t \quad (5.18) \]

Eq. (5.11) can be expressed for estimating the rise of sensible heat in incremental time period as
\[ del Q_{\text{sen}} = del Q_{\text{in}} - del Q_{\text{devol}} \quad (5.19) \]
New temperature of the particle can be estimated with the known rise in sensible heat and expression for the new droplet temperature is

\[ T_{pC}^{j+1} = T_{pC}^j + \left( \frac{\Delta Q_{sm}^j}{BL_{wt}^j \times CP_{BL}^j} \right) \]  \hspace{1cm} (5.20)

The model equations presented for both the transition phase and the devolatilization phase are simulated for determining the mass loss till the droplet touches the char bed by using MATLAB 7.1 and the results are presented in chapter 6. The flow chart showing the algorithm for solving the model equations is given in Figure 6.1b and 6.1c of chapter 6 and the results of simulation are presented in chapter 6.