Black Liquor Droplet Swelling Model during Pyrolysis

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Abstract. Black liquor is a spent pulping liquor from kraft pulping process. The concentrated black liquor is combusted or gasified to recover the chemical energy and to recycle the pulping chemicals. It undergoes several processes, i.e. drying, pyrolysis, and combustion and/or gasification. The droplet swells slightly during drying. Conversely, it swells heavily during pyrolysis. It can swell up to 20-30 time its original volume. The swelling stops when the pyrolysis reaction ends and/or when the solid loses its viscoelastic properties. Swelling phenomena also happens in other system, e.g. polymer foam moulding and coal pyrolysis. Two key phenomena for swelling behaviour are: gas production inside a material that forms gas bubbles and the material viscoelastic properties. The bubbles grow and whole droplet then swells accordingly.

Introduction

Black liquor is spent pulping liquor from kraft pulping process. It contains dissolved organic component and inorganic salts from pulping chemicals. Black liquor from a pulp digester has a solid content about 10-15%. This liquor is then concentrated in a series of evaporator to about 60-80% solid content. Conventionally, it is used as a fuel in a kraft recovery boiler. The liquor is combusted and heat is utilized to produce steam. The inorganic chemicals is collected as a molten salt in the bottom of the boiler and will be further processed to recycle the pulping chemicals. In a kraft recovery boiler, black liquor is sprayed to form fine droplets. The droplets then undergo several processes, namely: drying, pyrolysis, and combustion. Remaining water content in the droplets evaporates during drying. Next, pyrolysis reaction starts at about 200°C and it converts droplet solid into gases, condensable tars, and solid char.

Black liquor swells slightly during drying and swells heavily during pyrolysis (Frederick, Noopila, and Hupa 1991; Hupa, Solin, and Hyoty 1987). The whole droplet could swell up to 20 – 30 times of its original size (Frederick et al. 1991; Gea et al. 2003; Miller, Clay, and Lonsky 1989). The droplet swelling could affect its chemical reactivity due to the increasing surface area. As reported by Frederick & Hupa (1994), droplet that swelled more had higher rate of drying, pyrolysis, and char burning. In addition, the volume changes could also affect its trajectory inside a gasifier or boiler (Frederick et al. 1991).

According to Milanova (1988), two conditions were required to obtain high degree of swelling: i.e. gas production and formation of viscous matrix with plastic surface properties. Gas production from pyrolysis reaction could fulfilled the first requirement. Hence, the formation of the viscous material with plastic surface properties would be the critical factor. A mixture of two components in the black liquor, i.e. sucrose from cellulose or hemicellulose degradation and lignin, when softened by heating would behave as the required viscous plastic material (Milanova 1988; Miller et al. 1989). Pyrolysis gas filled or trapped inside voids of the viscous-plastic-matrix in the droplet. The pressure inside the voids
increased and the droplet expanded. Consequently, the swelling ended when the droplet was solidified and/or the gas production finished.

Black liquor specific properties and pyrolysis reaction condition could affect the swelling behavior (Chen et al., 2017; Frederick et al., 1991; Gea et al., 2003; Milanova, 1988; Miller et al., 1989; Murillo et al.). Some of those liquor specific properties were:

a. Liquor type. Kraft liquors commonly swelled extensively and sulfite liquors hardly swelled at all. However, even among the kraft liquor there were large differences in swelling (Frederick, 1997). This might be due to different raw material used and different pulping condition applied.

b. Liquor pH. The swelling of kraft liquors decreases considerably when pH was decreased (Frederick, 1997). Increasing the pH by addition of NaOH did not restore the swelling behavior. This irreversibility of the swelling behavior seemed to have its origin in irreversible changes of the lignin fraction in the organic matter. For sulfite liquors, their non-swelling behavior could not be altered by increasing the pH.

c. Organic/inorganic ratio. Inorganic chemicals decrease swelling moderately, but more than expected if the effect was solely due to dilution of the organic fraction (Frederick et al. 1991; Milanova 1988).

d. Aging of liquors. The swelling tendency decreased after aging of the liquors. It was also found that the aging effect was much higher for the liquor aged at higher temperature (Milanova, 1988).

Some reaction conditions that could affect the swelling were temperature, pressure and gas composition. The swelling decreased by increase of gas temperature surrounding the droplet (Frederick & Hupa, 1994). Frederick & Hupa (1994) also reported that the absence of oxygen in the gas surrounding the droplet could decrease the swelling. In addition, the presence of carbon dioxide, carbon monoxide, or water vapor would also decrease the swelling. The effect of pressure on swelling was reported by Whitty et al. (2008). It was found that higher the pressure would decrease the swelling volume significantly.

Empirical mathematical model of black liquor swelling has been proposed by previous researchers. Jarvinen et al. (2003) modeled the swelling as a stretching of uniform grid in a spherical droplet. Each cell in the grid swelled uniformly with the swelling coefficients that were experimentally determined. The proposed mathematical model was represented by equation (1) and (2).

\[
\beta = \left(1 + f_1(x_{dry}) \cdot (\beta_{dry} - 1) + f_2(x_{dev}) \cdot (\beta_{dev} - \beta_{dry})\right) \cdot (1 - x_c) \cdot (1 - \varphi^3)
\]

\[
\varphi = \frac{r_i}{r_o}
\]  

Where:
\(\beta\) = local volumetric swelling coefficient
\(\beta_{dry}, \beta_{dev}\) = volumetric swelling coefficients during drying and devolatilization
\(x_{dry}, x_{dev}\) = conversion of drying and devolatilization
\(r_i, r_o\) = radii of the spherical void and the droplet surface

Shurtz et al. (2012) proposed a simple empirical swelling model for coal pyrolysis that could be used in a CFD modeling. The model is described in equation (3).

\[
\frac{d}{d_o} = \left(\frac{m/m_o}{\rho/\rho_o}\right)^{1/3}
\]

Where:
\(d\) = droplet diameter
\(d_o\) = initial droplet diameter
\(m\) = droplet mass
\(m_o\) = initial droplet mass
\(\rho\) = apparent density
\[ \rho_0 = \text{initial apparent density} \]

Black liquor swelling models in equation (1) and (3) were empirical and it did not really have physical interpretation. For other system, i.e., polymer foam molding, more rigorous models that was based on theoretical study have been developed (Everitt et al. 2003; Hong, Fang, and Yao 2016; Mao, Edwards, and Harvey 2006; Ruiz, Vincent, and Agassant 2016; Tsivintzelis, Angelopoulou, and Panayiotou 2007; Venerus 2003; Wang et al. 2005). Foam was formed by a viscoelastic polymer contained a blowing agent. The blowing agent was dissolved gas that could be devolatilize, fill, and then expand the bubbles inside the polymer matrix, thus expanding the whole polymer. This process comparable with the black liquor swelling, the only difference was the source of blowing gas. It was from black liquor pyrolysis reaction instead of dissolved gas in foam. Black liquor droplet softened and became a viscoelastic matrix. The pyrolysis gas trapped, accumulated, and increased the pressure inside the bubbles. The bubble size grew and thus expanded the whole droplet (Frederick et al. 1991; Milanova 1988). Therefore due to the apparent mechanism similarity, the model developed for foam expansion may be applicable to be used for black liquor swelling.

Patel (1980) has developed a model to describe the growth of a bubble inside a viscous Newtonian liquid. Some important assumptions were: the bubble was spherical and isolated, the liquid phase was infinity and had Newtonian characteristic, the liquid viscosity was constant, the system was isothermal, gas-liquid equilibrium in the interface could be represented by Henry’s law. Figure 1 illustrated the schematic of bubble growth. The detailed equations derivation was presented by Patel (1980), and the final equation was presented in Equation (4).

\[ \frac{dR}{dt} = \frac{\left( P_G - P_L \right) \cdot R}{4 \cdot \eta} - \frac{\sigma}{2 \cdot \eta} \]  
\[ \text{Where:} \]
\[ R = \text{bubble radius} \]
\[ t = \text{time} \]
\[ P_G = \text{gas pressure} \]
\[ P_L = \text{liquid pressure} \]
\[ \eta = \text{viscosity} \]
\[ \sigma = \text{surface tension} \]

Other researchers have proposed other type of bubble growth models. Favelukis & Albalak (1996) proposed a model that took into account the non-Newtonian liquid. Mao et al. (2006) proposed two step bubble growth model: first step was for nucleation and bubble growth and second step was bubble growth only.

The aim of this study is to develop a mathematical model that can represent the swelling behavior of a single black liquor droplet during pyrolysis. However, the swelling phenomena is not an isolated phenomenon. The wet droplet undergoes drying prior to the pyrolysis. The heat and mass transfer into and from the droplet will also affect the swelling behavior. Therefore, to model the swelling of the black liquor droplet, all of those phenomena need to be taken into account. The modelling result will then be compared with the experimental data.
Mathematical Model

Droplet drying model

During drying, water inside the droplet diffuse out toward the surface. It was assumed the diffusion was only in radial direction. At the surface, the droplet evaporated into the surrounding gas flow. The mass of the droplet and its temperature can be calculated using Equation (5) and (6) that were derived from heat and mass balances in the droplet.

\[
\rho \cdot \frac{\partial \omega_w}{\partial t} = \rho \cdot D_w \cdot \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \omega_w}{\partial r} \right) \quad (5)
\]

\[
\rho \cdot \frac{\partial T}{\partial t} = k \cdot \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right) \quad (6)
\]

The initial conditions:

\[
\omega_w(r, 0) = \omega_{w0} \quad (7)
\]

\[
T(r, 0) = T_b \quad (8)
\]

The boundary conditions:

\[
\frac{\partial \omega_w}{\partial r}(0, t) = 0 \quad (9)
\]

\[
\frac{\partial T}{\partial r}(0, t) = 0 \quad (10)
\]

\[
\frac{\partial \omega_w}{\partial r}(R, t) = -\frac{\dot{m}_{wv}}{D_w} \quad (11)
\]

\[
\frac{\partial T}{\partial r}(R, t) = -\frac{h_w}{k} (T_s - T_{bulk}) \quad (13)
\]

Where:

| Symbol | Definition                  |
|--------|----------------------------|
| \omega_w | mass fraction of water     |
| T      | temperature                |
| t      | time                       |
| \omega_{w0} | initial water mass fraction content |
| \dot{m}_{wv} | water vapor evaporation rate |
| k      | conductivity               |
| D_w    | diffusivity of water in the droplet |
| h_w    | mass transfer coefficient of water vapor |
| h_T    | heat transfer coefficient  |
| T_s    | surface temperature        |
| T_{bulk} | gas bulk temperature     |

The droplet diameter was also changed during drying. The droplet diameter was assumed only due to density changes of the droplet and can be represented in Equation (14).

\[
d = \left( \frac{\omega_w}{4 \cdot \pi \cdot \rho} \right)^{\frac{1}{3}} \quad (14)
\]

The drying process was assumed to begin when the droplet enter the reactor and finish when its temperature reached the onset temperature for pyrolysis. In the droplet drying model, the mass changes of the droplet was calculated using equation (5) and its temperature was calculated using equation (6). The droplet initial mass and initial temperature were taken from experimental data. The boundary conditions used in the calculation were presented in equation (9)-(13). The mass transfer coefficient and
heat transfer coefficient of the spherical droplet were calculated using Sherwood and Nusselt number correlation, respectively (Mezhericher, et al, 2008).

\[
Sh_d = \frac{d_d \cdot h_m}{D_g} = \left( 2 + 0.6 \cdot Re_d^{1/2} \cdot Sc^{1/3} \right) (1 + B)^{-0.7}
\]

\[
Nu_d = \frac{d_d \cdot h_T}{k_d} = \left( 2 + 0.6 \cdot Re_d^{1/2} \cdot Pr^{1/3} \right) (1 + B)^{-0.7}
\]

\[
Re_d = \frac{\rho g \cdot v_g \cdot d_d}{\mu_g}
\]

\[
Sc = \frac{\mu_g}{\rho_g \cdot D_g}
\]

\[
Pr = \frac{C_p g \cdot \mu_g}{k_g}
\]

\[
B = \frac{C_p g \cdot (T_d - T_{fg})}{h_{fg}}
\]

Where:

- \(Sh_d\) = Sherwood’s number
- \(d_d\) = Droplet diameter
- \(h_m\) = Mass transfer coefficient
- \(Re\) = Reynold’s number
- \(Sc\) = Schmidt’s number
- \(B\) = Spalding’s number
- \(Nu_d\) = Nusselt’s number
- \(h_T\) = heat transfer coefficient
- \(k_d\) = Heat conductivity
- \(Pr\) = Prandtl’s number

It was assumed that the gas properties could be represented by the nitrogen gas since it was the majority in the gas constituent.

The droplet mass and temperature changes needed to be calculated while the droplet diameter was also changed as represented in equation (14). To accommodate this coupling partial differential equation with diameter changes, the numerical calculations were conducted per time step (\(\Delta t\)). At the first step, calculation is conducted from time \(t_0\) to \(t_1 = t_0 + \Delta t\) using initial water content of the droplet (\(\omega_{w_0}\)), initial temperature (\(T\)), and initial droplet radius (\(R_d\)). The partial differential equation was calculated using the \texttt{pdepe} function in MATLAB to obtain \(\omega_{w_1}\) and \(T\) at time \(t_1\). Once \(\omega_{w_1}\) was calculated, the droplet mass (\(m_d\)) was then calculated using equation (21) and its diameter (\(D_d = 2 \cdot R_d\)) was calculated using equation (14).

\[
m_d = 4 \cdot \pi \int_0^{R_d} \rho_d \cdot \omega_{w_1} \cdot r^2 \cdot dr
\]

The calculation was then continued to the second time step, i.e. for time \(t_1\) to \(t_2 = t_1 + \Delta t\), to calculate new value of \(\omega_{w_1}\) and \(T\). The initial conditions were from the previously calculated value of \(\omega_{w_1}\) and \(T\) together with the previously value of \(R_d\). These subsequent calculation was continued until \(T\) reach the onset temperature of pyrolysis (\(T_{onset}\)).

**Droplet pyrolysis model**

During pyrolysis, droplet solid material were converted into gas, tar, and char. The droplet would also swell due to gas product trapped inside the bubbles in the droplet. To model these phenomena, the simultaneous heat and mass transfer needed to be coupled with the model that represented the droplet size increase due to swelling.

Equation of continuity and equation of energy for the droplet became:

Gas and volatile:
\[ C_T \cdot \frac{\partial \omega_{gv}}{\partial t} = C_T \cdot D_{gv} \cdot \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \omega_{gw}}{\partial r} \right) + \tau_{pyro} \]  

Temperature:
\[ \rho \cdot C_P \frac{\partial T}{\partial t} = k \cdot \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right) + q_{pyro} \]  

Figure 2. Swelling due to bubble growth inside a black liquor droplet.

\[ \frac{dR}{dt} = \left( P_G - P_L \right) \cdot R \cdot \frac{R}{4 \cdot \eta} - \frac{\sigma}{2 \cdot \eta} \]  

Figure 2 illustrated the droplet swelling process. It was assumed that small bubbles were formed inside the droplet due to gas generation during pyrolysis. Gas was continuously generated during pyrolysis and trapped inside the bubble. Black liquor solid matrix surrounding the bubbles was softened due to the heat and behaved as viscoelastic material that easily swell. The accumulation of trapped gas would increase the pressure and the bubbles size expanded. The whole droplet would then swell. This bubble expansion was represented by equation (24). The driving force for the droplet radius \( R \) expansion was the difference between gas pressure inside the droplet \( (P_G) \) and surrounding gas pressure \( (P_L) \). Droplet viscosity \( (\eta) \) and surface tension \( (\sigma) \) were also affected the bubble expansion rate.

The partial differential equations (22) and (23) were coupled with the ordinary differential equation (24). Those equation could be solve numerically with initial and boundary conditions:

Initial conditions:
\[ \omega_{gw}(r, 0) = 0 \]  
\[ T(r, 0) = T_0 \]  

Boundary conditions:
\[ \frac{\partial \omega_{gw}}{\partial r}(0, t) = 0 \]  
\[ \frac{\partial T}{\partial r}(0, t) = 0 \]  
\[ \frac{\partial \omega_{gw}}{\partial r}(0, t) = h_w \cdot \left( \rho_{gw,s} - \rho_{gw,b} \right) \]  
\[ \frac{\partial T}{\partial r}(R, t) = - \frac{h_T}{k} \left( T_s - T_{bulk} \right) \]
The pyrolysis reaction was assumed to begin when the droplet temperature reach the onset temperature for pyrolysis. In this model, the reaction was simplified by assuming that only gas production that was taken into account. The tars that were produced were assumed to be trapped inside the droplet during swelling and thus did not released from the droplet and were incorporated in the char mass. The droplet swelling would change the droplet mass significantly and the general procedure for calculation were analogous with the drying calculation but with different mechanism of droplet radius increase.

At the end of drying stage, the droplet mass \( m_{d_j} \), droplet temperature \( T \), and droplet radius \( R_d \) were obtained from the calculation. This value became the initial value for pyrolysis stage modeling. Pyrolysis start at time \( t_{pyr} \), and calculation was conducted with time step \( \Delta t \). At the first step, i.e. from \( t_{pyr} \) to \( t_{pyr} + \Delta t \), gas fraction side the droplet was calculated using equation (22) and the temperature was calculated using equation (23). Black liquor pyrolysis kinetics were not conclusively available in the literature. The data that were available such as in (Bhattacharyya, Parthiban, and Kunzru 1986) only stated the mass decrease rate but not the gas production rate, therefore it could not be used in the model in equation (22). However, for coal pyrolysis some data were available to define the gas production rate. Since coal mostly contain carbon as in the black liquor, it was assumed that the reaction rate equation for coal could also be used for black liquor. Therefore in this calculation, the gas production rate from the pyrolysis would be assumed to follow the same equation as in the coal pyrolysis as in equation (31).

\[
\frac{d}{dt}m_{d} = A_{pyro} \cdot \exp \left( \frac{-1}{2} \cdot \frac{(T - T_{pyr})}{w_{pyro}} \right) \tag{31}
\]

Once the \( \omega_{gas} \) and \( T \) were calculate, droplet mass \( m_{d_i} \), and droplet radius \( R_d \) could be calculated using equation (32) and (24).

\[
m_{d_{i+1}} = m_{d_i} - 4 \cdot \pi \cdot M R_{gas} \cdot C_T \int_0^{R_d} \left( \omega_{gas_{i+1}} - \omega_{gas} \right) \cdot r^2 \cdot dr \tag{32}
\]

The coupling partial differential equations (22) and (23) were calculated using function pdepe in MATLAB. From equation (22) the gas fraction in the droplet could be calculated. This gas fraction was then converted to gas pressure by assuming ideal gas condition, using equation (33).

\[
P_g = \frac{n_g \cdot R_g \cdot T}{\frac{4}{3} \cdot \pi \cdot R_d^3} \tag{33}
\]

\[
n_g = \frac{\omega_{gas} \cdot \rho_d}{M R_g} \tag{34}
\]

The calculated gas pressure inside the bubbles in the droplet could be used to calculate the bubble diameter increase using equation (24) for the time step. Therefore in the end of the time step, the droplet mass, droplet diameter, and droplet temperature could be obtained. These values were then used as the initial conditions for calculation of the next step.

**Experimental Method**

**Materials**

Concentrated black liquor from a soft wood pulping process was used in this study. It was obtained from a pulp mill in Gothenburg, Sweden. The solid content in the concentrated black liquor was 66.0%.

**Methods**

The pyrolysis and gasification of black liquor involve many complex chemical reactions in addition to the physical processes. In order to study most of phenomena that occur during pyrolysis and gasification, a specially built thermogravimetric analyzer (TGA) for single droplet black liquor reaction has been constructed.

The TGA device holds three type of instruments: 1. gas flow controllers, to control the input gas to the TGA equipment; 2. gas heaters, to pre-heat gas input to the TGA to the desired temperature; 3. analyzing instruments that consist of: thermocouple to measure the temperature inside the droplet, an analytical balance to measure the droplet mass changes, a video recorder to visually observed the droplet
behavior, and gas analyzers to measure the outflow gas concentration. The gas analyzers can measure the concentration of \(\text{CO}_2\), \(\text{CO}\), \(\text{CH}_4\), \(\text{SO}_2\), and \(\text{H}_2\text{S}\). The general scheme of the TGA equipment can be seen in Figure 3.

During an experiment, a black liquor droplet with known mass was placed on the hook made by the thermocouple wire. The droplet diameter was adjusted to be about 2 or 3 mm. The droplet on the hook was then inserted into the TGA furnace that has been pre-heated to the desired temperature. For the pyrolysis experiments, nitrogen gas was used as the input gas.

Results and Discussion

Black liquor droplet that was heated in nitrogen atmosphere was assumed to undergo only drying and pyrolysis reaction. Figure 4-Figure 6 illustrated the comparison of calculation result and experimental data for temperature profile, mass changes, and diameter ratio changes for an experiment at 400\(^\circ\)C, respectively. For temperature, mass decrease and droplet radius expansion, the modeling result generally gave good agreement with the experimental data.

Temperature profile in Figure 4 provided a comparison between the calculated and the experimental data. In the model, the droplet radius was divided into several increments for discretization in the Finite Difference Approximation calculation. Each line in the curve represented each increment temperature. The outer diameter represented in the upper most curve or the relatively highest temperature in the profile. Vice versa, the center of the droplet is in the lowest curve which therefore showed the lowest temperature. In the drying region, it could be seen there were two distinctive region which represented the condition before and after the boiling point of the droplet. The lower part was the part before boiling, thus most of the heat was used for increasing the temperature, and the upper part was after the boiling point in which most of the heat was used for evaporating the water. The tip of thermocouple that were used to measure the droplet temperature located somewhere inside the droplet. Its location could not exactly adjusted since the droplet shape and size could shift when its viscosity decreased due to heating. However, the calculated temperature gave a good agreement compared to the measured values.
Figure 4. Temperature profile of calculation and experimental data for droplet drying and pyrolysis at 400°C.

In the Figure 5, the calculated mass droplet changes was compared with the experimental result. It seemed that even before the boiling point temperature was reached, significant amount of water has been evaporated. This indicated that the water vapor mass transfer from the droplet was high due to relatively high velocity of the hot gas flow surrounding the droplet. This condition indicated that the water behaved as a free liquid water before the boiling point temperature therefore it can evaporate freely to the bulk gas flow due to mass transfer. When the temperature reach its boiling point the water content has already been relatively low so that it behaved as bounded water that could not evaporate freely to the bulk gas flow due to binding with the droplet solid. Therefore it become a lot harder for the water to evaporate and thus the evaporation rate became slower.

Figure 5. Droplet mass profile of calculation and experimental data for droplet drying and pyrolysis at 400°C.

Figure 6 illustrated the comparison of swelling during drying and pyrolysis. The model could give a good agreement with the experimental data. It could be seen that the droplet swelled slightly during
drying as modeled due to density decrease and then swelled heavily during pyrolysis due to the trapped pyrolysis gas as modeled.

Figure 6. Diameter ratio of calculation and experimental data for droplet drying and pyrolysis at 400°C.

Conclusion
The mathematical model could provide the temperature, mass, and diameter changes of the black liquor droplet during drying and pyrolysis. Those calculated data in general gave good agreement with the experimental observation of temperature, mass, and droplet diameter changes during the process.

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