COMBUSTION OF BLACK LIQUOR DROPLETS

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INTRODUCTION

In conventional processes, black liquor is fired into recovery furnaces at solids contents ranging from 60-70% and at temperatures of 105-120°C. With high solids firing, the solids content may exceed 80% and the firing temperature 175°C (1). Spray nozzles form the liquor into a flat, conical, or elliptical sheets which quickly disintegrate into droplets. Black liquor sprays typically have a mean droplet diameter of 2-3 mm and a range from 0.5-5 mm. Droplet formation is discussed in more detail by Adams (2).

This presentation deals with the fate of liquor droplets after they have left the nozzle. First, the stages of droplet combustion are discussed, based on data from ongoing fundamental combustion studies in laboratory conditions. Then liquor-to-liquor differences in combustion behavior are compared, and their causes are discussed. Finally, the practical implications of burning characteristics to recovery boiler performance are considered.

THE STAGES OF COMBUSTION

The combustion of liquor droplets proceeds in four stages, as illustrated in Figure 1.

Drying

In the drying stage, most or all of the water in the droplet is evaporated. Drying takes 1-2 seconds for an average size droplet (3; Figure 2a), and the drying time increases in direct proportion to the droplet diameter (4). The droplet swells slightly, typically by a factor of 1.5 in diameter (Figure 3a), as it enters the furnace and begins to boil. It swells and contracts slightly as the liquor continues to boil, but does not swell more through the rest of the drying stage (5). The droplet temperature rises rapidly to about 150°C early during drying, and then increases more slowly, approaching 300°C at ignition (Figure 3b).

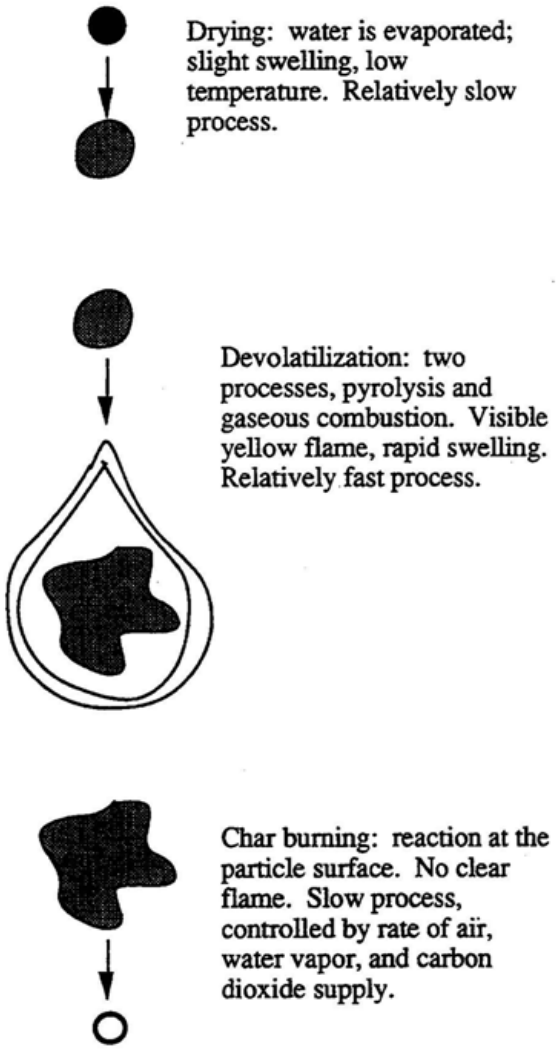


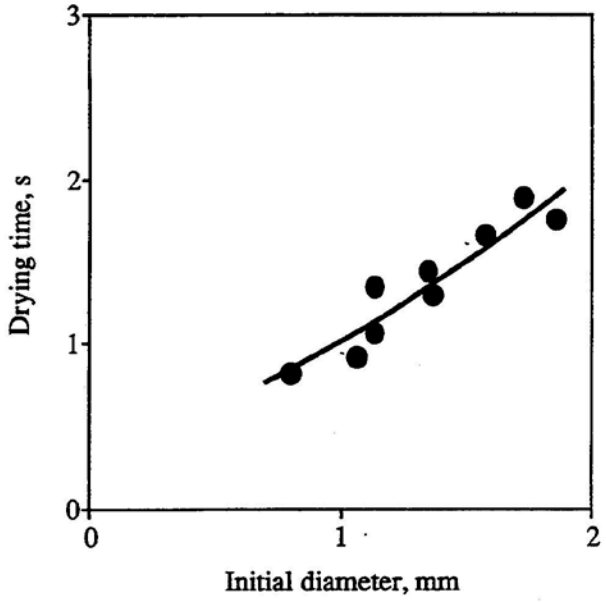
Figure 1. Black liquor burning stages

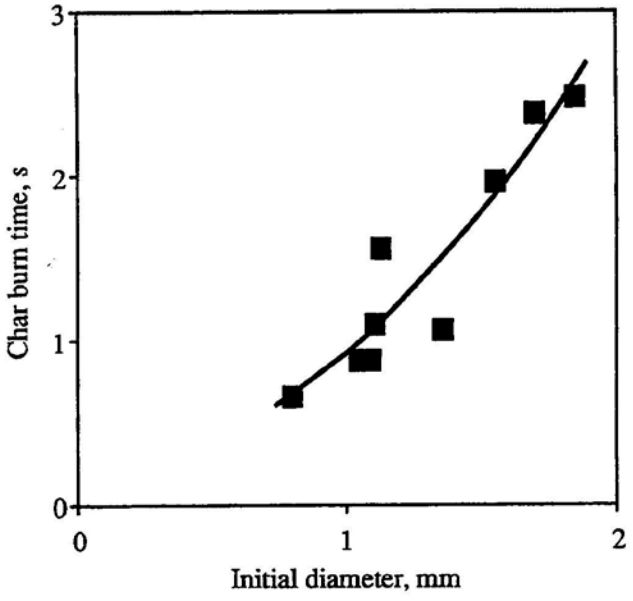
By the end of the drying stage, all visible signs of boiling have ceased. The droplets appear as extremely viscous or plastic, or as solid particles.

Devolatilization

For droplets burned in air, a bright, yellow flame appears at the droplet surface at the end of the drying stage. This marks the beginning of the second stage of burning, which involves pyrolysis of the liquor's organic matter and burning of the volatiles. The flame spreads rapidly, engulfing the entire droplet in less than 0.5 seconds.

Most kraft liquors swell considerably during devolatilization (Figure 3a). A typical liquor droplet swells to three times its initial diameter by the end of the devolatilization stage (Figure 2b). This corresponds to an almost 30-fold increase in volume.





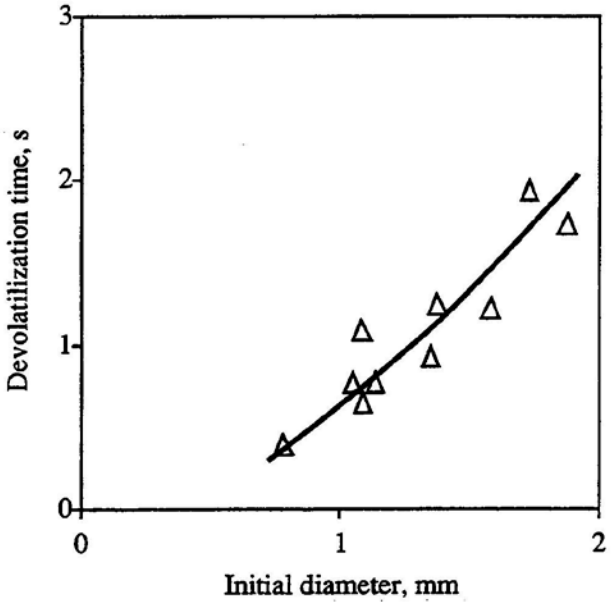


Figure 2. Combustion stage times versus initial droplet diameter for a kraft liquor, 60% solids, burned in air at 800°C. (a) drying, (b) devolatilization, (c) char burning.

During this stage, the temperature of the droplet rises rapidly (Figure 3b). At the end of the stage, the flame disappears, indicating that the droplet has lost all of its volatile organic matter. Devolatilization lasts typically 0.5-2 seconds in air for an average size droplet (3), but is slower at reduced oxygen content.

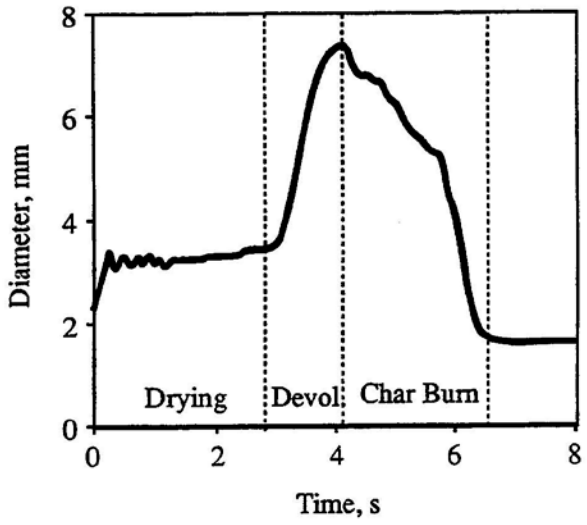
Much of the fume generation in recovery boilers may be during devolatilization. Our recent findings show that 15-30% of the sodium in black liquor is volatilized during this stage (15). This is enough to account for nearly all of the precipitator catch in most recovery boilers.

Char Burning

After the release of volatiles, the residue from the liquor droplet is a swollen, porous char particle containing mainly carbon and sodium salts. Although the sodium salts are molten, the particle is given a solid structure by the carbon particles it contains. The particle burns at its surface, and it shrinks in size (Figure 3a) as carbon is burned away. There is no visible flame during char burning, but only a glow at the hot char surface. Char burns as fast as oxygen is supplied to the particle surface. Air, CO2, and water vapor are all effective in converting char carbon to CO, which is burned in the surrounding gas.

The temperature of the char particle continues to rise during the char burning stage. In air, the temperature inside the particle may increase to 400°C above the ambient gas temperature (Figure 3b).

At the end of char burning, the carbon is depleted and the particle collapses suddenly into a molten droplet about half the diameter of the original liquor droplet. Char burning times vary from liquor to liquor, depending mainly on swelling and carbon content. Burning times are strongly influenced by the furnace gas composition; typical values in air are 1-6 seconds (Figure 2c).



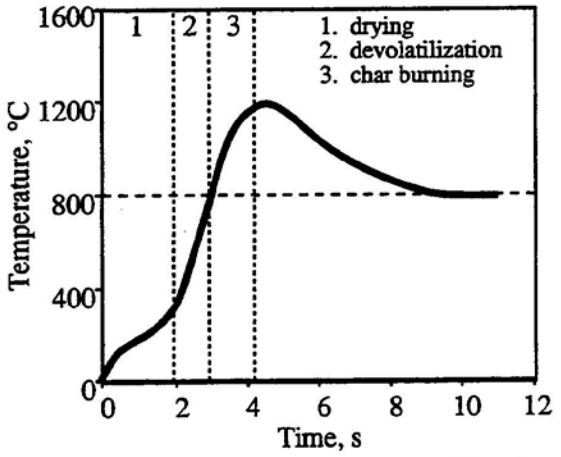


Figure 3. Diameter and temperature profiles for kraft liquor droplets burned at 800°C in air. (a) diameter versus time for a 2.2 mm droplet; (b) temperature versus time for a 1.5 mm droplet.

Some fume is released during char burning, particularly near the end of the stage. Also, small particles, about 0.1 mm in diameter, are often ejected from the burning char particle.

Inorganic Reactions

The melt formed at the end of the char burning stage consists of the inorganic constituents of the liquor. As char burning ends, the sulfur is completely reduced and the droplet contains Na_2S and Na_2CO_3. If the droplet is allowed to oxidize, the sulfide is converted to sulfate. This reaction is exothermic and may further increase the droplet temperature (Figure 3b). In normal recovery boiler operation, most of the char reaches the char bed before the char burning stage ends, and oxidation of sulfide is minimized. However, some droplets are entrained by the flue gases and carried to the upper furnace. These are gradually oxidized, forming carry over dust which contains Na_2SO_4 and Na_2CO_3 as main constituents.

A key question is where do each of these stages of combustion occur in a given recovery furnace with its particular liquor spray pattern? This will be discussed briefly at the end of this presentation, and in more detail in the presentations which follow this one.

BURNING OF DIFFERENT LIQUORS

Figure 4 shows the elapsed times for the stages of combustion of thirty liquors from different processes. The times are for droplets of the same size (1.5 mm diameter) at 60% solids, burned in air at 800°C. Twenty five of the liquors originate from kraft pulping processes using different wood species, one is a soda liquor, and the other four are from sodium based sulphite pulping.

The liquors differ widely in their burning behavior. The times drying and devolatilization vary by more than ±40% around the average values. The char burning times vary even more. Within the kraft liquors, the fastest burns more than twice as fast as the slowest. The sulphite liquor chars take almost twice as long to burn as the kraft chars. The soda liquor burned about the same as a typical kraft liquor.

The char burning times shown in Figure 4 are for droplets burned in air. In a recovery furnace, the char burning times will be 3-4 times as long because of the lower oxygen concentration. In terms of recovery boiler performance, char burning rate is the most important and the most variable of the combustion stages.

Figure 5 shows the maximum swelling for the same liquors as in Figure 4. Swelling is shown as the volume of the char at the beginning of char burning per gram of dry black liquor solids in the droplet prior to burning. Some of the liquors, particularly the sulphites, swell hardly at all. Others swell dramatically, to more than 50 cm^3/g black liquor solids. The highly swelling liquors are the ones which burn more rapidly. There is a strong inverse correlation between the char burning times in Figure 4 and the maximum swelling in Figure 5.

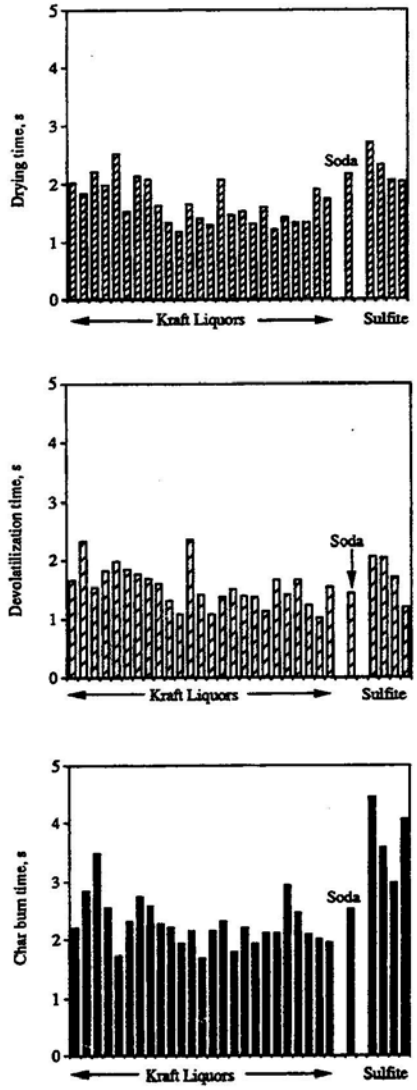


Figure 4. Combustion stage times for 30 liquors. (a) drying, (b) devolatilization, (c) char burning.

FACTORS WHICH INFLUENCE BURNING BEHAVIOR

Liquor-specific Factors

Before discussing the factors which influence burning behavior, it is important to examine the basic processes which control the rate for each stage. The drying and devolatilization processes are heat transfer controlled, while char burning is mass transfer controlled (4, 6-8). This means that droplets will dry and devolatilize as fast as heat is supplied to them. Char gasifies and burns as fast as oxygen is supplied. The oxygen source may be O_2, CO_2, and/or H_2O.

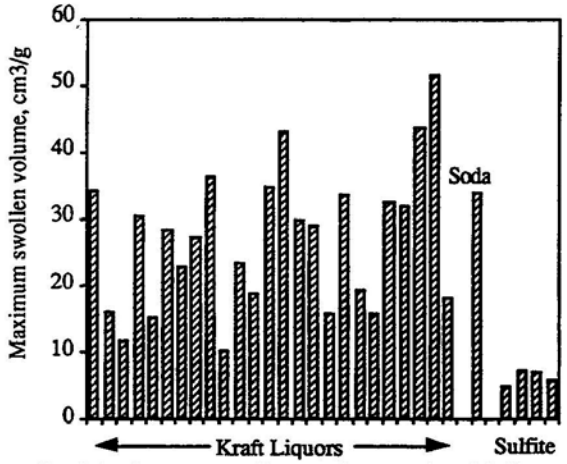


Figure 5. Maximum swollen volumes for 30 liquors burned in air at 800°C.

The rate of the heat and mass transfer processes which control burning all depend strongly on the diameter of the droplet or particle. For that reason, the most important liquor-specific factor in droplet combustion is swelling. During drying, different liquors swell much the same (5) which is why there are not greater differences in drying times in Figure 4. During devolatilization, droplets which swell more receive heat faster from the surrounding gas and flame, but the heat is conducted more slowly into the droplet. This accounts for the insensitivity of devolatilization time to differences in swelling. The strong correlation between char burning time and maximum swelling is observed because the char particles gasify and burn as fast as O_2, CO_2, and H_2O from the surrounding gases reach the particle surface. Particles with a greater external surface area therefore burn more rapidly.

Two other liquor-specific factors which impact burning times are the conditions required for ignition of the droplet and the fraction of the black liquor solids which is volatilized. Black liquor ignites when the rate of volatiles release reaches a critical value. Liquor-to-liquor differences in the rate of volatiles release as the droplet approaches dryness may account for the differences in drying times in Figure 4. While the factors which control ignition have been studied for other fuels, they have not yet been for black liquor, and the effect of differences in ignition behavior remain open to speculation.

The char burning time is inversely proportional to the volatile fraction in black liquor. The volatile fraction for most fuels depends on the carbon content of the fuel, the temperature to which the droplet is heated during devolatilization, and the heating rate. The organic and inorganic composition may also play a role.

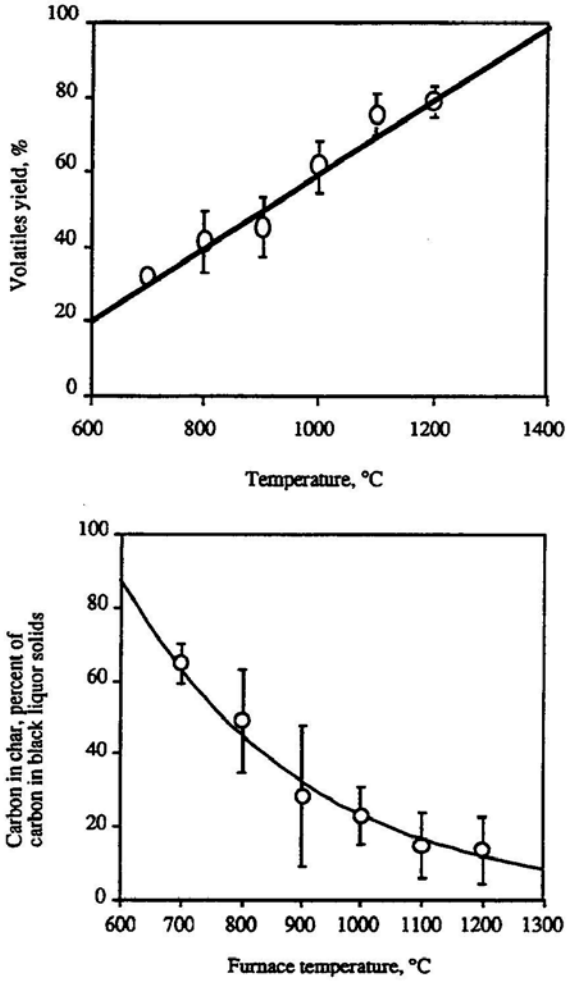


Figure 6. (a) Volatiles yield (a) and carbon content of char (b) versus temperature for a softwood kraft liquor. 6-55 mg droplets, 60-65% dry solids content, 10 s pyrolysis time. Error bars indicate ±1 standard deviation.

The effects of these variables on black liquor char burning time have not been studied until recently, but data now available shows that furnace temperature has a strong influence on volatiles yield (Figures 6; Frederick and Hupa, 1991). Research in this area continues.

Furnace Parameters

Furnace parameters, particularly temperature and gas composition, influence the combustion stage times differently. Since the drying rate is fixed by the heat transfer rate, drying times decrease rapidly as the furnace temperature increases (Figure 7). The surrounding gas composition has no influence on drying.

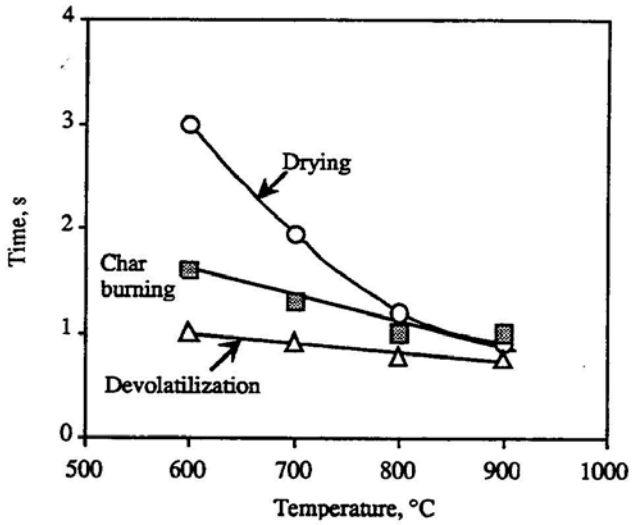


Figure 7. Combustion stage times versus furnace temperature for 1.5 mm droplets.

Devolatilization times are not affected much by furnace temperature because the flame surrounding the droplets isolates them thermally from the ambient furnace conditions. The flame temperature is the most important variable in determining the rate of devolatilization. It is most strongly influenced by the oxygen content of the surrounding gas.

Furnace temperature affects char burning times mainly because of its effect on the amount of carbon remaining to be burned after pyrolysis (Figure 6b). The composition of the surrounding gas is also an important furnace parameter in determining char burning time. As indicated earlier, the rate of char burning increases in direct proportion to the concentrations of oxygen, carbon dioxide, and water vapor in the surrounding gas. Char burning rates are not affected much by furnace temperature because they are controlled by mass transfer and mass transfer rates are not temperature sensitive.

FACTORS WHICH AFFECT SWELLING

As swelling is the most important liquor-specific variable which influences droplet combustion, we now take a closer look at the factors which affect it. As with combustion times, these can be divided into two categories, liquor-specific factors and furnace parameters.

Liquor-specific Parameters

The liquor-to-liquor variability in swelling has not yet been completely explained in terms of liquor composition and properties. The most obvious

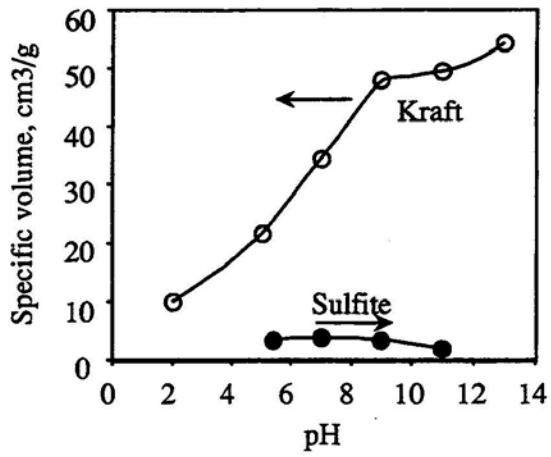


Figure 8. Effect of pH on swelling for kraft and sulfite liquors.

differences in swelling are between kraft and sulphite liquors (Figure 5). Part of the difference is related to pH. When kraft liquor is acidified with a mineral acid, its swelling behavior is clearly altered. As the pH is reduced to 7 and lower, swelling decreases dramatically, approaching that of a sulphite liquor (Figure 8). Increasing the pH of the acidified liquor with NaOH does not restore its swelling properties. The irreversible change in swelling behavior may be related to the loss of sulfide upon acidification, or to irreversible changes in the lignin fraction of the organic matter. Likewise, the practically non-swelling, slow burning behavior of sodium based sulphite liquors cannot be altered by raising the pH with either NaOH or Na_2CO_3.

The pH effect is particularly important to consider in cross recovery when kraft and NSSC liquors are mixed and burned together (3). The swelling and char burning behavior of mixtures of these liquors changes abruptly at 30-40% NSSC liquor based on dry solids (Figure 9). Below this level, the liquor mixture burns like a kraft liquor; above, it burns like an NSSC liquor. A pulp mill which operated near the transition point often had problems with sudden blackouts. When the NSSC/kraft liquor ratio was controlled more carefully, the blackout problem disappeared.

The relationship between the composition of black liquor and its swelling characteristics is not completely understood, but much progress has been made. The known effects are summarized here.

"Dead load" chemicals decrease swelling moderately. Figure 10 shows how the addition of "dead load", introduced in this case as Na_2SO_4, influences swelling.

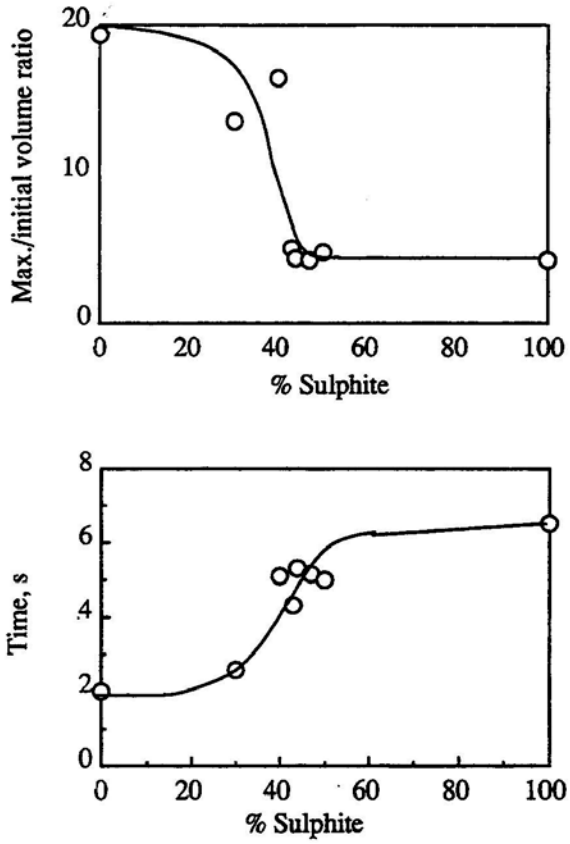


Figure 9. Maximum swelling and char burning times for mixtures of a kraft liquor and a sodium based sulphite liquor. Data are for 1.5 mm droplets at 60% solids burned in air at 800°C.

Swelling decreased more rapidly than expected if the effect is solely one of dilution of the organic solid fraction.

Large amounts of tall oil, when added to a strongly swelling liquor, can reduce swelling much more than expected from simply the dilution effect (Figure 10). The normal amount and variation of tall oil in black liquor have only a small effect on swelling, however.

The ratio of lignin/carbohydrate in black liquor can affect swelling. In studies with synthetic liquors, some exhibited a maximum in swelling at lignin/carbohydrate ratios near 50/50, while others showed no differences in swelling (17,18). Limited data indicates that lignin molecular weight also affects swelling (9)

Furnace Parameters

Gas temperature can affect swelling. The maximum swelling for three liquors at different furnace temperatures decrease by roughly a factor of two as temperature increases in the range 600-900°C (Figure

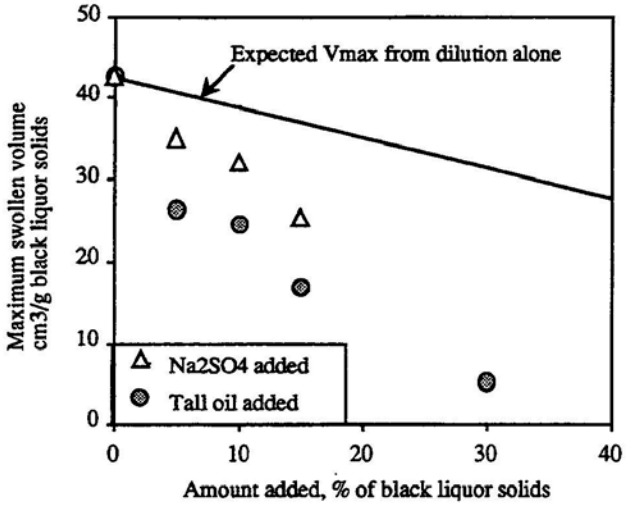


Figure 10. Effect of Na_2SO_4 and tall oil addition on maximum swelling for a kraft liquor burned in air at 800°C.

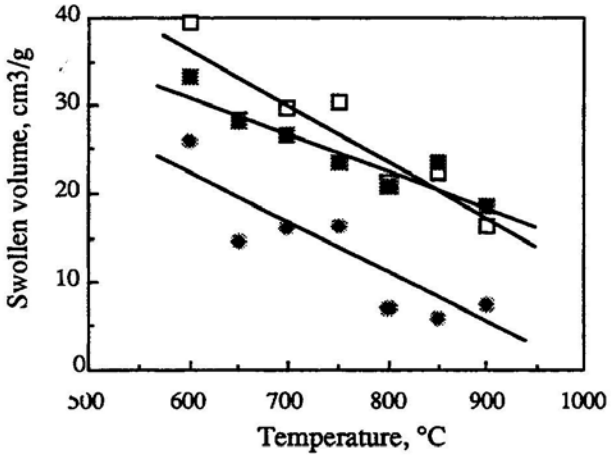


Figure 11. Effect of furnace temperature on swelling for three kraft black liquors burned in air

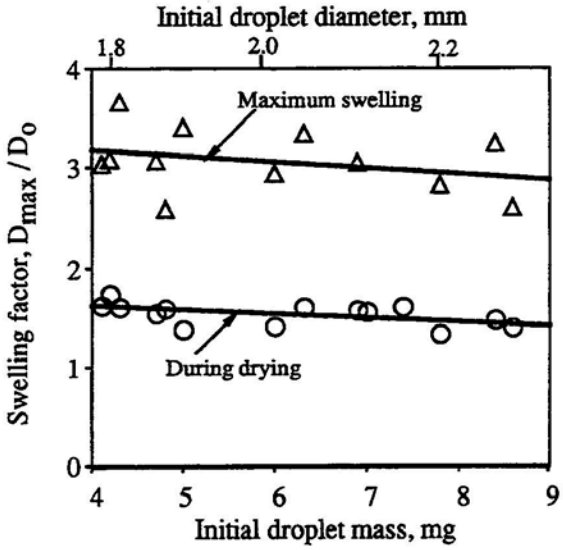


Figure 12. Effect of droplet size on swelling. Data are for a typical kraft liquor in air at 800°C.

11). At lower temperatures, much greater swelling has been observed (10, 11), but these conditions are not representative of recovery furnaces.

Swelling is nearly independent of droplet size when compared on a relative basis (Figure 12).

Table 1. The effect of gas atmosphere on the swelling of black liquor droplets at 800°C (4).

Gas composition	Swollen volume, cm^3/g
N_2	133±33
4-12% O_2	234±121
21% O_2	66±21
20% CO_2	43±4
20% H_2O	61±20

The data in Table 1 shows how furnace gas composition affects swelling. Under otherwise identical conditions, droplets swell less in air or high concentrations of CO_2 or water vapor. Swelling is greater in nitrogen and greatest at reduced oxygen concentrations.

COMBUSTION CHARACTERISTICS OF HIGH SOLIDS LIQUORS

With the current interest in high solids firing, a key question is how combustion behavior differs at high solids firing conditions. The combustion stage times and maximum swelling are shown for a typical kraft liquor in Figures 13-14. The measurements were made with droplets of constant initial mass but different dry solids content, at 800°C in air. The combustion stage times depend on the amount of water or dry solids in the droplet, so drying time is plotted as drying time per mg water initially in the droplets, while devolatilization and char burning times are plotted per mg dry solids.

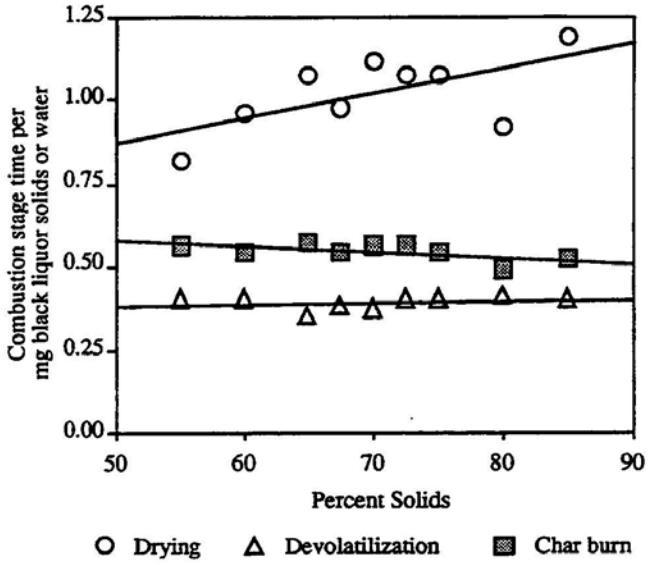


Figure 13. Effect of solids content on combustion stage times for 2.2 mm diameter droplets burned in air at 800 °C (14).

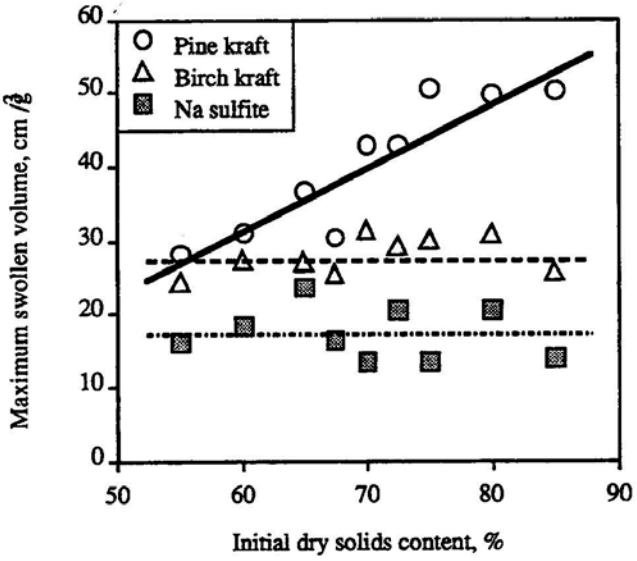


Figure 14. Effect of solids content on maximum swelling for 2.2 mm droplets burned in air at 700°C (14).

From this data, we see that there is very little difference in the basic burning characteristics at high dry solids content. The devolatilization and char burning times per mg dry solids change very little as initial solids content increases (Figure 13). The drying time per mg water is slightly longer at higher solids content. Swelling per mg dry solids is independent of initial solids content for some liquors but increases with dry solids content for others (Figure 14).

This data shows that the combustion behavior of black liquor droplets does not change greatly as dry solids content is increased. Because the droplets dry faster at higher initial dry solids content, it should be possible to use a coarser spray. This has the advantages of moving combustion lower into the furnace and reducing carry over. With this method of firing, more air will need to be delivered through the primary ports. A key remaining question is the effect of high solids firing on temperature in the lower furnace and its implications to fuming rates and plugging of gas passages with fume, precipitator efficiency and stack opacity, NO_x emissions, and corrosion in the lower furnace.

IMPLICATION TO DROPLET TRAJECTORIES AND BURNOUT

The swelling characteristics of black liquor have a great impact on the trajectory of a droplet in a recovery furnace. This in turn affects where heat is absorbed (during drying) or released (during the burning stages). It also impacts where burnout occurs and where deposits may form in the superheater.

The flow and temperature fields in a recovery boiler are very complex, and calculation of droplet trajectories is a slow and difficult task (12). However, insight into how swelling impacts droplet trajectory and burnout can be gained by examining the trajectories of droplets in a simple flow field.

Figure 14 shows the trajectory of a black liquor droplet in an upward flowing gas at uniform velocity. The trajectory was calculated using droplet combustion stage models to calculate the drying, devolatilization, and char burning times, and a momentum balance to calculate the velocity. The stages of combustion are marked by different symbols in Figure 15. Note that the upward motion of the droplet begins during drying, and continues part way through char burning. The trajectory is, of course, strongly influenced by gas velocity and initial droplet mass. At higher velocities, the downward motion at the end of char burning may not occur.

The effect of swelling on droplet trajectory and burnout is seen in Figure 16. This figure shows the calculated trajectories and burnout point for five liquors, varying from poorly to highly swelling, in a high velocity gas flow. The poorly swelling liquors burn slowly, but is carried upward more slowly by the gases because it

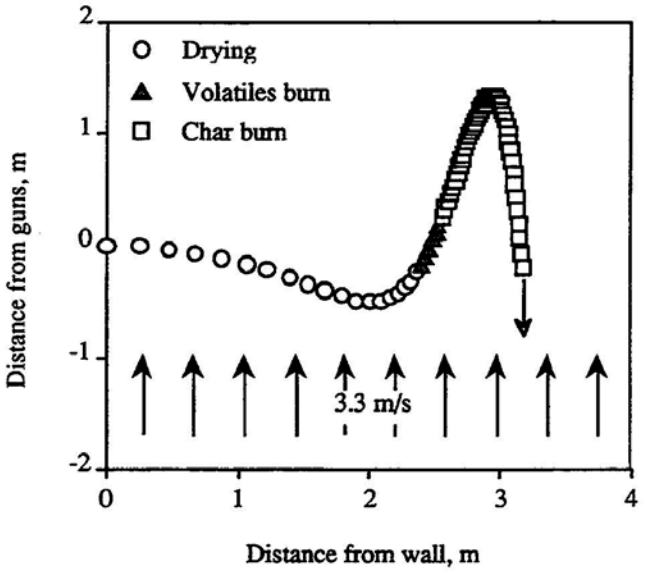


Figure 15. Trajectory for a 1.5 mm black liquor droplet at 60% solids, burned at 800°C in air flowing upward at 3.3 m/s. Maximum swollen volume = 24 cubic centimeters/g black liquor solids.

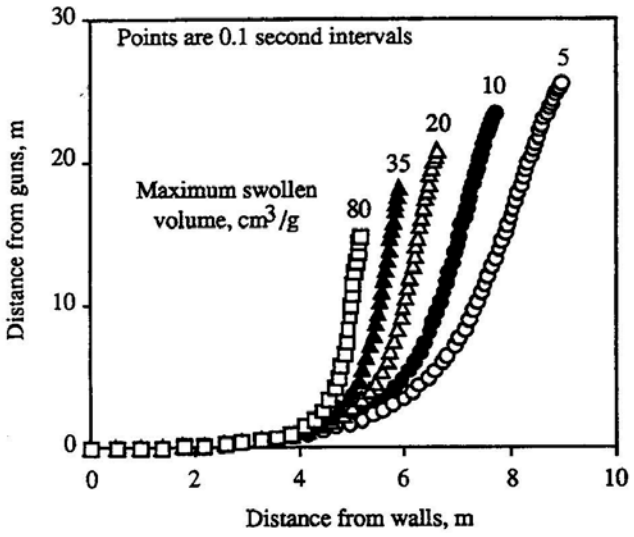


Figure 16. Effect of swelling during drying on trajectories to burnout for 2.2 mm droplets in an upward flowing gas at 1000°C. 10 m/s gas velocity, 5% oxygen in gas, 60% initial solids content.

remains relatively dense while burning. The highly swelling liquors move up rapidly with the gas, but burn even more rapidly. They burn out at a lower elevation than do more poorly swelling liquors.

The results in Figure 16 illustrate the complex interaction between swelling, burnout, and trajectory. The trajectories shown depend strongly on gas velocity and droplet size as well as on swelling. Of course the simplified patterns are not truly representative of furnace conditions. However, they do show at least qualitatively how swelling can impact burnout location and plugging of air passages.

CONSEQUENCES

Black liquor droplets burn in three distinct phases: (I) drying, (II) devolatilization, and (III) char burning. At furnace conditions, devolatilization is rapid and drying is somewhat slower. Char burning is much slower, and dominates the total burning time. In modern firing systems, the drying and devolatilization phases take place in flight, although larger droplets may continue to devolatilize in the char bed. Part of the char burning, perhaps as much as half, also occurs in flight.

Part of the liquor, usually the smaller droplets, may burn completely in flight. These are often entrained in the flue gas as "carry over" particles. The tradeoff between burning time and entrainability means that liquors with high swelling characteristics are not necessarily a greater carry-over problem than poorly swelling liquors. The upward gas flow rate varies across a recovery boiler, with the highest velocity in a central core (6). All liquors should be fired in a way that minimizes entrainment in the upward central core flow.

Kraft liquors from different processes show great variations in their combustion behavior. This is an important factor to keep in mind when transferring operating strategies from one unit to another. Good firing practices in one unit may not be successful in another if the liquor burning characteristics are greatly different.

Swelling is the liquor-specific combustion property which most affects combustion and combustion stability. It varies widely from liquor to liquor, but can be characterized by laboratory measurements. Swelling characteristics should be compared based on measurements made at furnace conditions, not at low temperatures. There is no correlation between low temperature swelling behavior and swelling at furnace temperatures (5).

The combustion behavior of high solids liquors is about the same as at lower solids. When firing high solids liquors, spray size needs to be reduced to offset the longer char burning times which result from the higher dry solids mass per droplet.

Burning sodium based sulphite or NSSC liquors together with kraft liquors may change the burning characteristics of the kraft liquor abruptly when the proportion of sulphite liquor exceeds 30% of the total dry solids.

The swelling characteristics and burning behavior of black liquor is affected by large concentrations of tall oil or extremely low pH. Both decrease swelling. Upsets which result in short-term, high soap concentrations or high ClO_2 generator brine inputs may cause boiler upsets and combustion instability.

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