

Role of the sulfate-sulfide cycle in char burning: experimental results and implications

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ABSTRACT A substantial fraction of the total burning load can take place on the surface of the char bed. Reduction is an inherent part of the char burning process and is not jeopardized by combustion air impinging on the bed. Quantitative, predictive equations for char burning agree well with experimental measurements of char particle burn times. Measured draft char burning rates were much higher than those corresponding to typical boiler design hearth loadings, suggesting a large potential for increased bed burning rates. There are two keys to increased bed burning: (a) providing an adequate supply of combustion air to the whole bed surface, matching the stoichiometric requirement of the fuel landing on the bed and (b) maintaining high temperatures in the bed surface zone. If these two requirements are met, all chemical functions in the lower furnace will take care of themselves.

Char burning

Burning of a drop of black liquor in air occurs in three distinct stages: drying, volatiles burning, and char burning (1). These are depicted and described in Fig. 1. Char burning is the last stage in the burning process and occurs as a heterogeneous reaction between the char particle and the oxygen in the combustion air. There is no visible flame, but rather an intense glow at the reacting surface. The residual carbon burns away, and the inorganic salts are reduced and melted out. Char burning does not tend to begin until the production of volatiles ceases, permitting oxygen to reach the char particle.

Burning times of drops of black liquor are strongly influenced by the size of the liquor drop and the nature of the air-drop contact. For drops of the size range normally encountered in the furnace burning in air, burn times are about 5-10 s. Drying and char burning stages tend to be the slowest (1).

Char characteristics

Char is the residual solid product from black liquor pyrolysis. It is a black, porous, friable material containing essentially all of the sodium and about one-half the carbon in the incoming black liquor. For most purposes, char can be considered to consist of three inorganic salts: sodium carbonate, sodium sulfide, and sodium sulfate, along with carbon and bound hydrogen.

From a chemical standpoint, carbon is the dominant species in the char. Carbon is the excess reactant. There is more than enough carbon present to reduce all of the sulfate to sulfide. Conversely, there is not enough oxygen present in the sulfate to burn off the carbon. Most of the oxygen needed to burn off the carbon in the char must come from combustion air. Hydrogen is minor and can be ignored for most purposes.

The most significant parameter governing the stoichiometric air requirement for char is the relative

proportion of carbon monoxide (CO) and carbon dioxide (CO₂) in the product gas. About twice as much air is needed if the char carbon is burned to CO₂ rather than CO. The air requirement for char burning is about 25-45% of the air required for burning all of the black liquor, depending on the CO-CO₂ split. Limited measurements of the gas composition just above the bed in a recovery furnace show a CO-CO₂ ratio of about 1:2. This proportion would correspond to a char air requirement of about 40% of the theoretical air required by the liquor solids.

Char burning is an exothermic (heat releasing) reaction. The heating value of char in a bomb calorimeter is about 4500 Btu/lb char. The effective heating value of char in the furnace will be lower than this because of the net reduction of sulfate that occurs and because some CO will be formed. Heating values under various conditions for a representative kraft char are:

- Bomb calorimeter (fully oxidized products): 4380 Btu/lb
- Smelt fully reduced, all CO₂

3430 Btu/lb

- Smelt fully reduced, all CO: 910 Btu/lb.

Bed burning

Char is the residual solids after black liquor pyrolysis. It is not the material landing on the char bed. Char formation is an inherent step in the burning of black liquor. When the black liquor solids pyrolyze and the pyrolysis gases burn, char is formed. This event can occur as droplets rise or fall in the furnace, on the wall, or in the char bed. Char burning takes place after char is formed and oxygen (from air) has an opportunity to reach the char. This can occur (and mostly does occur) on the char bed, but it can occur in flight, on the walls, etc.

Char burning and burning in the char bed of the recovery furnace are not identical. Char burning (a process) is the last stage in the black liquor burning process. Where it takes place in the furnace is dependent on operating conditions. Some char burning always occurs on the bed, but it may also occur as the particle falls to the bed or as it is swept upward with the combustion gases. Bed burning, on the other hand, includes all of the processes occurring in and on the bed in the furnace. These processes include char burning, but they may also involve volatile burning and even drying. In an individual, small liquor particle, the processes tend to occur sequentially. Within the furnace, large numbers of particles are involved at various stages in the burning process, tending to blur the distinctions between the process steps.

Sulfate-sulfide cycle

Kraft char burns via a sulfate-sulfide cycle. The carbon in the char reacts with sulfate, reducing it to sulfide and forming CO₂ and CO. The sulfide in turn reacts with oxygen from the combustion air, reforming sulfate and completing the cycle. The sulfate-sulfide cycle acts to carry oxygen to the carbon, which is burned off. The importance of the sulfate-sulfide cycle is that it permits simultaneous sulfate reduction and carbon burnup in the presence of an oxygen-containing atmosphere as long as the rate-limiting step during char burning is oxygen mass transfer to the burning char.

Description

Figure 2 illustrates the concept of the

sulfate-sulfide cycle. Oxygen comes in from the combustion air and reacts with sulfide (Na₂S), oxidizing sulfide to sulfate (Na₂SO₄). The sulfate carries the oxygen over to the carbon, where it reacts to form CO₂ and CO. The sulfate, in turn, is reduced back to sulfide, completing the cycle.

The cycle can operate at any concentration of sulfur or at any average reduction state in the system. The operating sulfur reduction state, or the reduction efficiency, during char burning is determined by the relative rates of sulfide oxidation and sulfate reduction. If the rate-limiting step is the oxidation of sulfide by air (e.g., an oxygen mass-transfer limit), the carbon will react with sulfate as fast as it is formed and keep the concentration of sulfate low (a high reduction efficiency). Conversely, if the rate-limiting step is the reaction between sulfate and carbon, the sulfide will be oxidized as fast as it is formed, and the sulfide

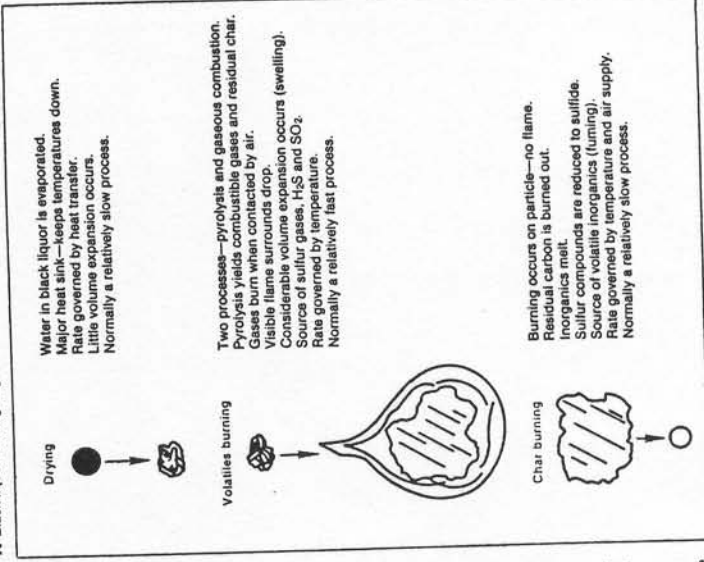
concentration would be low (a low reduction efficiency). Simultaneous carbon burning and sulfate reduction can occur if the rate-limiting step is the oxidation.

Significance

The significance of the sulfate-sulfide cycle is that it permits two apparently contradictory processes, carbon burnup and sulfate reduction, to take place simultaneously in the furnace. It is entirely possible to burn off char carbon in an oxygen-containing atmosphere while still achieving high degrees of sulfur reduction. The only necessary condition is for the rate of the carbon-sulfate reaction to exceed the rate of oxygen supply.

The carbon-sulfate reaction rate increases exponentially with increasing temperature. The high temperatures required to ensure a high enough carbon-sulfate reaction rate tend to be self-generated because char burning

1. Black liquor burning stages.



(even with net overall reduction) is an exothermic process. It is not necessary to maintain a gaseous reduction zone (oxygen deficient atmosphere) in the lower furnace in order to get good reduction. In fact, starving the lower furnace for air is counterproductive because it results in low bed temperatures and lower rates of reduction.

Quantitative analysis of char burning

The sulfate-sulfide cycle can be treated quantitatively. The following assumptions are made:

1. The only significant chemical species in the char are C, Na₂S, Na₂SO₄, and Na₂CO₃.
2. Fume formation and sulfur gasification are neglected.
3. The only gaseous species of interest are O₂, CO₂, and CO.

The second assumption is useful because it makes Na₂CO₃ and total alkali a constant and also makes the sum of Na₂S and Na₂SO₄ constant. This is a good first approximation for treating char carbon burnup and sulfate reduction. Even though fuming is significant in a recovery furnace, its effect on carbon burnup and reduction is minor. Sulfur gasification occurs before char is formed.

The composition of the char is then completely specified by three variables:

$$[C] = \text{moles char carbon/mole Na}_2\text{S}$$

$$r = \text{reduction efficiency} = \text{Na}_2\text{S}/(\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4) \text{ (in moles)}$$

$$[S] = \text{moles S/mole Na}_2\text{S}$$

Note that [S] is constant by assumption, and only two variables, [C] and r, are functions of time.

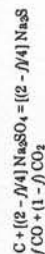
The following reactions are considered to take place.

1. The only reaction between char species and O₂ is:



Define R₀ as the rate of this oxidation in moles O₂/mole Na₂S.

2. Char carbon is oxidized by sulfate according to the reaction:



where f is the mole fraction of CO in the product gas. Define R_c as the rate of this C-Na₂SO₄ reaction in moles C/mole Na₂S.

Material balances (in moles) can be written per unit mole of alkali. Only two material balances are needed. Balances for carbon and sulfate totally describe the system. (Na₂CO₃ doesn't change and Na₂SO₄ is known if Na₂S is known).

The carbon balance is:

$$R_c = -d[C]/dt \quad (1)$$

The sulfate balance is

$$[(2 - f/4)R_c - (R_0/2)] = [S](d[r]/dt) \quad (2)$$

Carbon-sulfate rate

The rate of reaction between sulfate and three different types of carbon (pulverized graphite, kraft char, and soda char) was found to be represented by Eq. 3. This was determined in a laboratory pool reactor described in Refs. 2 and 3.

$$d[SO_4]/dt = -k_1([SO_4]/(k_2 + [SO_4]))^{0.5} \exp(14771/(1.477R)) \quad (3)$$

where

[SO₄] = sulfate concentration

[C] = carbon concentration

k₁, k₂ = rate constants

T_R = reference temperature

= 1200°K

ΔT = temperature difference

= T - 1200°K.

Best fit values for the parameters in Eq. 3 are given in Table I.

A key feature of the carbon-sulfate rate behavior is that the rate is independent of sulfate concentration for all reduction efficiencies up to 95%. Sulfate concentration does not have a major effect on the reaction rate until reduction efficiencies exceed 99%.

Sulfide oxidation rates

Sulfide oxidation in molten carbonate is an inherently fast reaction. In experiments in which air was bubbled through molten carbonate containing sulfide, the oxygen was consumed as fast as it was supplied until low sulfide concentrations were reached. The break occurs at about 0.1 mole/L, which corresponds to a reduction efficiency of 2% in a typical smelt.

These results indicate that sulfide oxidation would be controlled by oxygen mass transfer under almost any

circumstances. Control would shift to inherent chemical kinetics only when the sulfide is essentially depleted.

If the oxygen supply is limited by mass transfer, we might have

$$R_0 = k_0 A P_{O_2}$$

where

k₀ = oxygen mass transfer coefficient, moles O₂/area time atm

A = contact area between oxygen supply and char, area/mole Na₂S

P_{O₂} = oxygen partial pressure, atm

Predicted behavior

A predictive set of equations for burning kraft char can be developed using the rate constants in Table I and assuming f = 0 (no CO produced). These equations can be solved numerically. Figures 3 and 4 show how the carbon content, reduction state, and particle mass vary with time for two cases. Values of the parameters are shown on the figures. The temperature value should not be taken too literally. The mass-time curves show four distinct zones:

1. An initial rapid drop as the sulfate originally present in the char is reduced
2. A constant rate of drop-off as carbon is burned off under oxygen-limited conditions (at a fixed, high state of reduction)
3. A period of weight gain as sulfide is reoxidized to sulfate
4. A final falling rate period of exponential decay as the final carbon is burnt out in a fully oxidized melt.

Experimental verification

The experiments on the burning of single particles of char were carried out on a specially designed apparatus we call the "single particle reactor." This reactor is designed to provide a direct measurement of mass changes as a char particle reacts. The particle is suspended from a sensitive microbalance and is continually exposed to a convective gas stream of controlled temperature and composition. The composition of the gases leaving the reaction zone can be monitored. A viewing port allows us to observe and photograph the burning particle. A coiled wire and pan help to support the burning particle and retain the smelt.

The particle is suspended from the microbalance in the area of the view-

ing port. Typical particles contain about 0.1-0.2 of black liquor solids or char and are about 1/4 in. in diameter. Swollen char particles have dimensions of 0.5-1.0 in. Preheated gas (N₂, air, etc.) passes through a flow straightener and downward over the reacting particle. Gas flowing in this direction helps keep fume and other combustion products out of the microbalance. A by-pass arrangement with dampers is used to stabilize gas flow and temperature before the gas is passed over the particle.

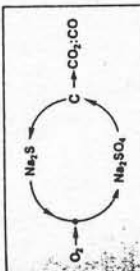
Burning rate curves

The prime measurement of burning rate in the char particle experiments was the particle weight as a function of time. A large number of experimental burns were carried out. A typical result for kraft char burning in air

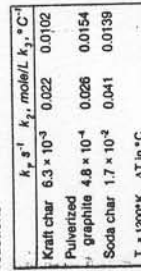
O₂ case. Total burn times ranged from 25 to 30 s. Again there is a weight gain at the end arising from sulfide reoxidation. The behavior in this case is also in close agreement with predicted behavior. Oxygen-limited burning rates would be expected to be proportional to the oxygen concentration.

A typical weight vs. time curve for burning a soda char particle in air is shown in Fig. 7. The times for all weight changes for soda char are about the same as for kraft char, 10-20 s. However, this is a bit misleading because some residual carbon remained at the end of the burn. A particle lattice of carbon would not burn out, probably because of the coupling between low rates, low heat production, and temperature. In contrast to the kraft char, no weight gain was observed at the end of the burnout

2. Schematic of sulfate-sulfide cycle.



3. Calculated burning curves.



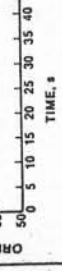
4. Calculated burning curves, mass vs. time. (T = 2420°F, [C]₀ = 3, r₀ = 0.5, [S] = 0.34)

5. Rate parameters for carbon-sulfate reactions

reactions	k ₁ , s ⁻¹	k ₂ , mole/L	k ₃ , °C ⁻¹
Kraft char	6.3 × 10 ³	0.022	0.0102
Pulverized graphite	4.8 × 10 ⁴	0.026	0.0154
Soda char	1.7 × 10 ⁴	0.041	0.0139

T_R = 1200°K, ΔT in °C.

6. Kraft char particle burning in 10% O₂ (initial mass, 110 mg. Kraft char. Gas flow, 98 L/min. 10% O₂ and 90% N₂. Temp., 885°C. Linear rate, 0.43%/s.)



7. Soda char particle burning in air. (Initial mass, 90 mg. Soda char. Air, 100 L/min. Temp., 890°C. Linear rate, 1.1%/s.)



Black liquor

with soda char, confirming that the weight gain at the end of char burns arises from sulfide oxidation.

Addition of Na_2SO_4 to the soda char (16% based on the initial black liquor solids) resulted in a weight gain at the end of the burn and eliminated the residual carbon matrix at the end of the burn. In other words, adding sulfate to the soda char before the burn caused the system to behave like a kraft char.

Interpretation

All of these results on the single particle reactor are consistent with the predictions of the theory of the sulfate-sulfide cycle and with the fundamental work on reduction and oxidation. The linearity of the weight-vs.-time curves and the similar "total burn times" between kraft char and soda char are what would be expected for a process controlled by O_2 mass transfer. The variables influencing the mass transfer rate lie mainly outside the particles and hence are not changed as burning proceeds. Visual evidence also confirms a mass-transfer-controlled burn. The reaction initiates at the leading edge of the particle where the air impacts the particle, and burning proceeds down along the particle as the top portion burns away. Burning remains most intense at the top of the particle.

The weight gain at the end shows that sulfur is present in a reduced state as burning proceeds. This is in accordance with predictions from the analysis of the sulfate-sulfide cycle. The sulfur remains in a reduced state until the carbon becomes depleted, and then the reduced sulfur oxidizes. The weight gain at the end of the oxidations of kraft-char and soda char with sulfate (and the absence of a weight gain with soda char) can only be interpreted as arising from the reoxidation of sulfide.

The concentration of O_2 in the convective gas stream flowing past the particle had a pronounced effect on kraft-char burning. The burning rate was reduced at lower O_2 concentrations. For 10% O_2 , the time for complete burnout ranged from 25 to 30 s. When burning was carried out with only 2% O_2 , the rate was slow, and burn times exceeded 60 s. For a mass-transfer-controlled process, one would expect the burning rate to be related to the O_2 concentration, and that seems to be what is observed in these experiments.

Implications on operation

The results of this work can be used to provide an overall view of how black liquor burns in a recovery furnace. The two most significant findings in this respect are:

1. Kraft char burns via a sulfate-sulfide cycle. This permits reduction to occur simultaneously with carbon burnup, even though sizeable quantities of oxygen reach the char.
2. Char burning is an exothermic reaction. Heat release on the burning char bed can provide the heat needed to maintain the bed temperatures required by the temperature-sensitive reaction rates.

It is not necessary to maintain an oxygen-deficient atmosphere above the char bed to achieve satisfactory reduction efficiencies. Adequate reduction can be obtained as long as bed temperatures are high enough and there is an excess of carbon in the bed. The chemically active region of the bed is that portion where the char has access to oxygen from the combustion air. Char reactions in the absence of oxygen tend to be self-limiting, since they are endothermic, and the reaction rates decrease rapidly as temperature decreases.

In our view, a substantial fraction of up to 60% of the total combustion should occur on the bed, along with a demand for a corresponding amount of the total air to be supplied to the bed. The capability to burn large amounts of combustible material on the bed permits operations with coarse sprays (which minimizes entrainment). All that is required is an adequate supply of combustion air to the bed and sufficiently high bed temperatures.

Burning rates

Typically, design firing rates in a recovery furnace correspond to about 2.0-2.5 lb dry solids/ft² of floor area/min. Our work indicates that a 4-in.-thick reaction zone at 1700°F (or a 2-in.-thick zone at 1800°F) is capable of handling the entire char burning load at design firing rates. This suggests there is ample opportunity to increase bed burning rates.

There are two basic requirements for increasing the burning rate on the char bed. First, the required amount of air to satisfy the stoichiometric needs of the bed material must be supplied under conditions that suffi-

ciently high mass transfer rates are attained. Second, the reacting zone on the bed surface must be kept at a sufficiently high temperature. Air-bed contact must be maintained over the entire bed surface in proportion to the amount of fuel landing on any particular area of the bed. Bed temperatures are increased by increasing the fuel value of the material landing on the bed, increasing burning rates, and by keeping all heat sinks (e.g., wet liquor) away from the bed.

Reduction

High reduction efficiencies should be relatively easy to obtain. Reduction rates depend on the temperature and carbon content of the char. Reduction is a relatively rapid reaction. Given enough carbon, reduction can be completed with a residence time of a few minutes at 1700°F and within a few seconds at 2100-2200°F. Reduction rates can always be increased by increasing temperature. If low reduction efficiencies are caused by low reduction rates, the cure is to increase the surface temperature of the bed. This temperature can be increased most readily by increasing the air supply to the bed to increase the burning rates.

Low reduction efficiencies in the furnace can also be caused by sulfide reoxidation before the smelt runs out of the furnace. The bed plays a protective role here, by providing a path for molten reduced smelt to move out of the active surface layer and away from the combustion air. A properly sized and shaped char bed can shield the smelt from the primary air. Any time combustion air comes in direct contact with molten smelt, some re-duction efficiency is being lost.

The most important parameter for optimizing the processes occurring in the lower furnace is bed temperature. More specifically, it is the temperature in the thin, air-accessible, surface layer of the bed. Higher temperatures increase the potential burning rate and provide for better reduction efficiencies. Higher burning rates on the bed increase the tolerance for handling coarse sprays, which should lead to less entrainment.

Air and fuel distribution

If the bed surface temperature is kept hot enough (we believe it should be at least 2000°F), the chemical recovery functions in the furnace tend to take care of themselves. No other special actions need to be taken to achieve

acceptable reduction, sulfur scavenging, and low residual carbon in smelt. The main additional requirement is to introduce the black liquor in such a way that all of the sodium salts end up on the hearth (minimum entrainment).

With the chemical functions thus self-established, the combustion process can be treated in essentially the same manner as it is for any other fuel. Each element of black liquor fuel has a requirement for a certain amount of air. The essence of good combustion control is to introduce the fuel (black liquor) and air into the furnace in such a manner that the air reaching a given location is proportional to the stoichiometric demand of the fuel at that location.

This requirement implies that the black liquor spray system and the air supply system should be coupled. The distribution of air to the bed must match the distribution of char landing on the bed. If most of the char is landing close to the walls, most of the air is needed near the walls. If the char is spread uniformly over the bed surface, the combustion air to the lower furnace should also be distributed evenly over the bed. Changes in liquor spray patterns without a parallel adjustment in air distribution will always result in less than optimum performance.

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