Abstract

The yields of char residue, fixed carbon, and inorganic carbonate were measured for oxidized black liquor char residues produced in a laboratory laminar entrained-flow reactor (LEFR) at heating rates of 4000–13,000°C/s. The char residue yields at the end of devolatilization thus obtained decreased nearly linearly with temperature, from 75% at 700°C to 58% at 1100°C. There were explainable differences in the char residue yields from the liquor used in this study and those used in other studies. Char residue yields seemed to depend mainly on the temperature to which the particles or droplets were exposed and were not very sensitive to heating rate. Fixed carbon yields behaved similarly to those of the char residue. The fixed carbon remaining at the end of devolatilization decreased from 67% at 700°C to about 45% at 1100°C. The carbonate content in black liquor changed very little before and after devolatilization.

Keywords: Black liquor; Biomass; Char; Pyrolysis; Gasification

1. Introduction

Black liquor is a biomass waste from the chemical pulping of wood. It consists of alkali lignin, polysaccharides, wood extractives, and residual inorganic pulping chemical. It is burned as a fuel in the paper-producing countries of North America, Northern Europe, Asia, and South America. The inorganic residue, mainly sodium and sulfur compounds, is recovered, converted back to active pulping chemicals, and reused. The composition range of black liquors from North American and Nordic wood species is shown in Table 1.

The organic matter in black liquor solids begins to degrade thermally above 200°C, producing water vapor, CO₂, CO, hydrogen, light hydrocarbons, tar, and light sulfur-containing gases (Kubes et al., 1982; Bhattacharya et al., 1986; Söderhjelm et al., 1989; Li and van Heiningen, 1991; Gairns et al., 1994; Sricharoenchaikul et al., 1997). For the relatively large (2–3 mm) droplets fired in black liquor burning, devolatilization is essentially complete when the residue temperature reaches 650–750°C (Hupa et al., 1987; Frederick et al., 1994). The char residue contains fixed carbon, some hydrogen, and most of the inorganic matter.

The char residue yields from the pyrolysis of solid fuels vary widely depending upon fuel characteristics and process conditions. The char residues from coal and biomass fuels are normally reported on an ash-free basis. Black liquor yields much more ash residue than coal or most other biomass fuels, typically 35–45% of the dry solids mass. Further, the inorganic residue from pyrolysis or combustion is nearly all relatively volatile sodium salts – chloride, sulfate or sulfide, and carbonate (Reis et al., 1995). In this work, we refer to the solid residue from pyrolysis as char residue. This includes the ash as well as carbon and other elements that remain from the organic matter originally in the liquor. The mineral-ash-free char residue is referred to as char, the fixed carbon in the char residue as fixed carbon, and the carbon remaining as carbonate in the char residue as the carbonate carbon. Char carbon refers to the sum of the fixed and carbonate carbon in the char residue.

For coals pyrolyzed at temperatures greater than 600°C, char residue yields typically range from 35% to 70% on a dry, mineral-ash-free basis. The distribution of carbon between volatile gases and char residue is determined by kinetic and stoichiometric factors. The yield...
of carbon as volatile gases during devolatilization increases with increasing reaction temperature and the fixed carbon yield decreases (e.g., Anthony et al., 1975; Kobayashi et al., 1977; Solomon and Colket, 1979; Suuberg et al., 1979). Char residue yield data obtained for pyrolysis to the same final temperature but at different heating rates indicate at most a minor effect of heating rate (Sprouse and Schuman, 1981; Niksa et al., 1984).

For biomass fuels, char residue yields are much lower than with coals because of the higher oxygen content of biomass. The char residue yield from rapidly pyrolyzed cellulose is less than 5% for pyrolysis temperatures above 400°C (Hajallgol et al., 1982; Scott et al., 1988). Char residue yields are higher for lignocellulosic materials, typically between 10% and 25% on a mineral-free basis for rapid pyrolysis at temperatures above 500°C (i.e., Scott and Piskorz, 1984; Scott et al., 1988).

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For black liquor, data on the distribution of pyrolysis products between volatile matter and char residue are very limited. Bhattacharya et al. (1986) pyrolyzed low-sulfur black liquor solids in ceramic boats to final temperatures of 620–740°C. They reported char residue yields of 48–52%. Gairns et al. (1994) reported char residue yields for 20 mg droplets of kraft black liquor pyrolyzed in N$_2$ at temperatures from 500°C to 900°C. The yields decreased from 70% at 500°C to 65% at 700°C, but then dropped to 41% at 800°C. McKeough et al. (1995) reported char residue yields of 49–75% from the pyrolysis of 100 mg of dried black liquor in a heated-grid reactor at temperatures from 400°C to 900°C. Fixed carbon yields were not reported in any of these studies.

Frederick et al. (1994) measured char residue and char carbon yields from 2–3 mm droplets of a kraft black liquor pyrolyzed for 10 s in a nitrogen atmosphere at temperatures from 700°C to 1200°C. Their conditions corresponded to heating rates of the order of 100°C/s. Their char residue yields decreased with increasing temperature, from 68% at 700°C to 21% at 1200°C. The amount of carbon initially in the black liquor that remained as carbon in the char residue decreased from 66% at 700°C to 18% at 1200°C. In similar experiments with six kraft liquors at 800°C, the carbon in the char residue ranged from 26% to 48% of the carbon originally in the black liquor solids.

Whitty et al. (1997) measured volatiles yields from 15 different black liquors using four different laboratory-scale reactors. They reported volatiles yields between 23% and 34% from nine different kraft softwood black liquors using a single-droplet tube reactor at 900°C and atmospheric pressure (10 and 13 mg droplet size), which correspond to char residue yields of 66–77%. Their char residue yields decreased on an average by 2.5% per 100°C temperature rise from 700°C to 900°C. They obtained lower char residue yields (8.8% decrease per 100°C temperature rise) with a pressurized grid reactor (1 MPa, 850–1100°C, 3000°C/s heating rate) with a 10 mg sample of black liquor.

The objective of this work was to determine the effect of temperature on char yield and carbon remaining in black liquor char residue following rapid pyrolysis. In the work reported here, experimental measurements of char yield and carbon in black liquor char residue were made using a 90–125 μm size fraction of dry black liquor particles at heating rates of 4000–13 000°C/s in a laminar...
entained-flow reactor (LEFR). At these conditions, temperature variations were negligible within the particles. Additional measurements were made with low heating rate (100°C/s) pyrolysis experiments with single droplets of black liquor (2 mm droplet size), using the same black liquor as the one used in the LEFR experiments.

2. Methods

2.1. Laminar entrained-flow reactor

Pyrolysis experiments with black liquor were conducted in a laboratory-scale LEFR. This type of reactor has two features that are important when obtaining fundamental pyrolysis and combustion data: it provides very rapid heating, and it uses particles that are small enough that temperature gradients within the particles are small.

A schematic of the experimental reactor is shown in Fig. 2. The LEFR consists of a vertical three-zone high-temperature electrical furnace with two ceramic tubes inside. It operates with a downward flowing gas stream at temperatures up to 1150°C and laminar conditions. The primary flow, a low-temperature gas stream, is injected at the center of the reactor. The secondary flow is preheated to reactor temperature and injected coaxially with the primary flow. The small particles are entrained in the primary gas flow. They are heated rapidly (4000–13 000°C/s) by the high-temperature secondary gas and by radiation from the hot walls of the reactor. After passing through the reactor, the particles and gases enter a water-cooled, gas-purged collector where they are quenched with cold nitrogen to stop the chemical reactions. After the quench, the particles larger than 3 μm in diameter (char residue) are removed by a cyclone, and the fine particles are collected on a nylon membrane filter (0.5 μm pore size) located upstream of the exhaust duct. Residence times of 0.3–2.0 s were achieved in the experiments reported here.

In each LEFR run, the reactor was preheated with nitrogen at the desired secondary-gas flow rate. At the beginning of each run, the particle feeder was started so that the primary gas and particles began to flow through the reactor. The duration of each run was 3–5 min, long enough to ensure that steady state had been achieved. At the termination of each run, the cyclone was sealed and removed to a nitrogen-purged glove bag. Its contents were weighed, and a portion of the material was transferred to a volumetric flask for extraction with water and analysis of the dissolved inorganic ions. The glove bag was necessary to prevent the extremely reactive char residue from oxidizing or combusting spontaneously on exposure to air.

In the experiments reported here, an oxidized southern pine kraft black liquor, obtained from a pulp mill in Georgia, was dried, pulverized in a jar mill, and screen sieved. The 90–125 μm fraction was collected and used in the experiments. The composition of the dry black liquor solids is shown in Table 2.

In the single droplet experiments, concentrated black liquor (2 mm droplet size) was placed on fine wires and

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Elemental composition (in wt%) of the dried black liquor solids for liquors used in this and other studies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Study</td>
<td>This work</td>
</tr>
<tr>
<td>Liquor type</td>
<td>Pine kraft</td>
</tr>
<tr>
<td>Carbon</td>
<td>34.90±0.07</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.10±0.31</td>
</tr>
<tr>
<td>Oxygen</td>
<td>35.10</td>
</tr>
<tr>
<td>Sodium</td>
<td>22.70±1.14</td>
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<tr>
<td>Sulfur</td>
<td>2.90±0.15</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.62±0.30</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.67±0.03</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.11±0.01</td>
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*By difference.
inserted into a heated quartz tube purged with nitrogen (heating rate ~100°C/s) and held for 10 s. The droplet was then removed and weighed for char residue yields.

2.2. Chemical analysis

Portions of the char residue from LEFR experiments were analyzed for carbon content at the Weyerhaeuser Company analytical laboratory in Tacoma, WA. Char residues from single droplet experiments were analyzed for carbon content by the Chemical Analysis group at IPST or by the Central Analytical Laboratory at Oregon State University. The concentration of carbonate in the char residue was measured by extracting the char sample with deoxygenated water under nitrogen and analyzing the resulting solution. The analysis was performed using a Dionex Model CES-1 capillary electrophoresis system (CES) with a conventional fused-silica capillary (50 µm capillary ID, 50 cm length, 20 kV separation voltage, and 210 nm detection wavelength). All the injections were hydrostatic and performed by raising the sample vial 100 mm above the level of the destination vial for 30 s. Dionex cation and anion electrolyte buffers were used. A more detailed description of the analytical procedures is provided by Sricharoenchaikul (1995).

3. Results and discussion

Devolatilization occurs very rapidly when black liquor solids are heated to temperatures substantially above 200°C. Typical experimental data for char residue collected in pyrolysis experiments in an LEFR are shown in Fig. 3 (Sricharoenchaikul et al., 1997). The data, for 90–125 µm particles heated at rates of 4000–13,000°C/s, indicate that devolatilization is complete essentially as fast as heat can be supplied to the particles. Generally, significant mass loss (30–50%) is measured at shortest residence time – additional loss occurs at a much slower rate. The relatively small incremental decrease in char residue collected after a reaction time of 0.3 s indicates that the loss of volatile gases via pyrolytic decomposition of the organic matter is complete in less than 0.3 s. Further loss of char residue mass is attributed to the formation of CO and CO₂ via sulfate and carbonate reduction, as shown in Eqs. (1)–(3) (Cameron and Grace, 1985; Li and van Heiningen, 1990).

\[ 2C + Na_2SO_4 \rightarrow Na_2S + 2CO \]  
\[ 4C + Na_2SO_4 \rightarrow Na_2S + 4CO \]  
\[ 2C + Na_2CO_3 \rightarrow 2Na (v) + 3CO \]

Particle temperatures versus residence time as predicted by Verrill and Wessel (1995) and by a detailed computational model for entrained-flow reactors that was originally developed by Flaxman (1986) are shown in Fig. 4. The latter model was modified by Littau et al. (1994) to account for the swelling and mass loss characteristics of black liquor. The calculations are for the same conditions at which the data in Fig. 3 were obtained. The difference between the predictions of these two models, especially at longer residence times and higher furnace temperatures, is due to the inclusion of detailed black liquor chemical reactions by the Verrill and Wessel model, which results in the overall exothermic behavior of the black liquor burning process as seen in the figure. The times for completion of pyrolysis at each temperature were estimated based on (a) the thermogravimetric analysis of Li and van Heiningen (1991), who showed that pyrolysis of black liquor was complete by 460°C at heating rates of 20°C/min, and (b) the correlation of Solin and Hupa (1984) for 2–3 mm black liquor droplets at heating rates of the order of 100°C/s. The small particles used in this study would have heated more uniformly than the larger, 2–3 mm droplets. Therefore, devolatilization would have been complete somewhere between 460°C and the higher limit predicted by the Solin and Hupa correlation (560°C and 870°C for furnace temperatures of 700°C and 1100°C, respectively). According to Fig. 4 (Verrill and Wessel model), devolatilization would have been complete in less than 0.08 s at 700°C and less than 0.04 s at 1100°C. These estimates indicate that the loss of volatile gases produced by the pyrolytic decomposition of the organic matter in black liquor is complete before the particles reach their final temperature, and that this process would be complete long before the shortest particle residence time for the data in Fig. 3 (0.3 s) was reached.

An important difference between the pyrolysis behavior of the small particles in Fig. 3 and those of the 0.5–5 mm black liquor droplets typically fired in recov-
ery boilers is that the temperature within the particles should be more uniform within the smaller particles. The temperature profiles shown in Figs. 5 and 6 were calculated by Verrill and Wessel (1995) using their detailed particle-burning model for black liquor. The profiles show that the temperature variations within the 100 μm particles used in this study are negligible. However, steep temperature gradients occur within the larger droplets typical of kraft recovery boilers. This indicates that devolatilization tends to occur in an outer shell of expanding thickness for the larger droplets, while a core of colder, unpyrolyzed material remains within. By contrast, devolatilization occurs much more uniformly throughout the smaller particles used in this study.

The char residue yields immediately after the release of the volatile pyrolysis products are shown in Fig. 7. The values from the LEFR experiments with the 90–125 μm fraction of particles was obtained by extrapolating the data in Fig. 3 and similar data at intermediate temperatures to zero residence times. Since the time required for devolatilization to be completed in the LEFR was always less than 0.08 s for furnace temperatures higher than 700°C, the pyrolysis residue yields obtained by extrapolation to time zero are a close approximation to the yields at the end of devolatilization. The char residue yield decreases with higher reactor temperature, from about 75% at 700°C to 58% at 1100°C.
Results from low heating rate experiments with the same black liquor are also included in Fig. 7. The low heating rate experiments were made with single droplets (2 mm diameter), pyrolyzed on fine wire hooks in a hot furnace environment for 10 s. The char residue yields from these larger particles decrease steadily with temperature, from about 100% at 400°C to 63% at 800°C. The high yields at lower temperatures suggest that the particles may not be heated to the furnace temperature within 10 s and that the devolatilization process was still in progress at the time the droplets were taken from the reactor. However, at higher reactor temperatures, above 600°C, in which the devolatilization should already be complete by 10 s, the residue yields show consistent agreement with data generated from LEFR experiments. This comparison indicates that char residue yields are not very sensitive to heating rate.

Three other sets of data, obtained with different black liquors, are also included in Fig. 7. Two of these are from single-droplet studies. Frederick et al. (1994) exposed 2–3 mm diameter black liquor droplets to a furnace environment containing 95% N₂/5% CO for 10 s, then removed, weighed, and analyzed them for carbon. Gairns et al. (1994) exposed droplets of a similar size to a furnace environment containing helium for 60 s before removing and weighing them. McKeough et al. (1995) placed about 100 mg of dried black liquor (particle size < 105 μm) in a heated-grid reactor in a nitrogen environment for 10–30 s, then removed, and weighed the residue to determine the char yield. The compositions of these three liquors are represented by the ranges given in Table 2.

The char residue yields from the studies shown in Fig. 7 fall into three categories. The first category includes the char residue yields from the fine (~100 μm) particles, and from 2 mm droplets for which pyrolysis was complete but carbon oxidation by Na₂SO₄ and Na₂CO₃ was not significant. These points fall within the gray band in Fig. 7. The second category includes the 2 mm droplets pyrolyzed for times too short and/or temperatures too low for pyrolysis to reach completion. The points at 400°C and 500°C from this study in Fig. 7 fall within this category. The third category includes the 2 mm droplets pyrolyzed at temperature high enough and times long enough for carbon to be oxidized by Na₂SO₄ and Na₂CO₃. The points from Frederick et al. (1994) and McKeough et al. (1995) at 900°C and higher (pyrolysis for 10 s) and the point from Gairns et al. (1994) at 800°C (pyrolysis for 60 s) fall within this category.

The gray band in Fig. 7 represents a more accurate residue yield versus temperature for the black liquor. For all the points within that band, pyrolysis was complete and the reduction of Na₂SO₄ and Na₂CO₃ proceeded too slowly to contribute significantly to the loss of carbon from the char residue. The uncertainty in the experimental measurements is ±5% of the initial black liquor solids mass. This is very nearly the same as the width of the gray band in Fig. 7. This analysis suggests that there is relatively little difference in char residue yield among black liquors. This finding agrees with that of Whitty et al. (1997), who reported similar differences for 15 black liquors pyrolyzed in N₂ at 700°C and 900°C for 15 s.

The total carbon in the char residue versus time and the carbon remaining as carbonate in the pyrolysis residue at the end of devolatilization are shown in Figs. 8 and 9, respectively. The total carbon versus time data are similar to the char residue data for the 90–125 μm fraction of particles – the carbon content of the char residue decreases rapidly during devolatilization (t < 0.3 s). It continues to decrease, but at a slower rate, after devolatilization is complete. However, the carbonate content of the char residue remains constant or decreases slightly during devolatilization (t < 0.3 s). It
subsequently increases to a maximum and decreases with longer particle residence times. Formation of carbonate may occur via thermal decomposition of sodium phenolates and salts of organic acids in black liquor. Reactions of alkali sulfur with CO₂ and/or H₂O also lead to the formation of carbonate. Some of these reactions are shown in Eqs. (4)–(7) (Gairns et al., 1994; Li, 1989; Sricharoenchaikul, 1995). Consequently, carbonate can be decomposed by reduction with carbon, producing sodium vapor and CO (Eq. (3)).

\[
\text{Na}_2\text{S} + 2\text{HCO}_2\text{H} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{S} + \text{CH}_2\text{O} \quad (4)
\]

\[
\text{Na}_2\text{S} + 2\text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{COS} \quad (5)
\]

\[
\text{Na}_2\text{S} + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{S} \quad (6)
\]

\[
\text{Na}_2\text{S}_2\text{O}_3 + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{SO}_2 + \text{S} \quad (7)
\]

Since there is little or no change in the carbonate in the char residue during devolatilization, the carbon as carbonate in the black liquor solids (4.7% of the carbon in the black liquor solids for the liquor used in this study) provides a good estimate of the carbonate carbon content of the char residue immediately after devolatilization is complete.

The total and fixed carbon in the char residue immediately after devolatilization was complete versus reactor temperature are shown in Fig. 10. The total carbon data of Frederick et al. (1994) are also included in Fig. 10. The trends for LEFR experiments are similar to those for the char residue yields – the carbon decreases with increasing furnace temperature but seems to approach an asymptotic value near 50% at higher temperatures. As with the pyrolysis residue yield data in Fig. 7, the carbon remaining in the larger droplets continues to decrease as temperature increases. Part of the mass loss in single-drop experiments at temperatures of 800°C and above may be caused by the oxidation of pyrophoric char upon removal from the reactor. This was not expected to be a problem for chars produced at lower temperatures (400–500°C).

In Fig. 7, it was shown that, except for the data at the higher temperatures in each set, the pyrolysis residue yields from the studies by Frederick et al. (1994), Gairns et al. (1994), and McKeough et al. (1995) from 400°C to 800°C follow the extrapolated trend of the LEFR data from 700°C to 1100°C. The pyrolysis residue yields from these researchers that fall well below the data from the present study were obtained at conditions where loss of carbon and other elements from the char residue would be expected. The mechanisms include loss of sodium and CO or CO₂ via reduction of Na₂CO₃ with carbon (Li and van Heiningen, 1990), reduction of sodium sulfate by carbon (Cameron and Grace, 1985), vaporization of NaCl and KCl (Cameron, 1987), and, possibly, shedding of char residue fragments (Verrill and Nichols, 1992). These processes occur in the pyrolysis residues after devolatilization is complete, and they contribute to the loss of carbon and inorganic matter (Reis et al., 1995). Wág et al. (1995) modeled these processes and their impact on char residue mass and composition following the devolatilization of black liquor. Based on Wág’s results, the magnitude of the mass loss from the pyrolysis residues after devolatilization at 800°C for 60 s or at 900°C and above for 10 s would account for the differences between the data from the present study and those of Gairns et al. (1994) and Frederick et al. (1994). When these points are not considered, the pyrolysis residue yields from the three liquors seem to decrease slowly with increasing pyrolysis temperature.

Based on data in Figs. 7 and 10, it appears that black liquor char residue and char carbon yields may not decrease significantly with increasing furnace temperatures above 1000°C, and that they are not very sensitive to heating rate in the range 100–10 000°C/s.
4. Conclusions

Char residue yields from pyrolysis of black liquor, when measured at the end of devolatilization and before char residue reactions proceed significantly, decrease with increasing reactor temperature. Char residue yields seem to depend mainly on the temperature to which the particles or droplets are exposed, and are not very sensitive to heating rate above ~100°C/s. Fixed carbon yields, when measured the same way, also decrease with increasing reactor temperature but level off above 1000°C. For the liquor used in this work, the fixed carbon yield was 67% at 700°C and 45% at 1100°C. There is very little change in the carbon present as carbonate before and after devolatilization.

Acknowledgements

This work has been supported by the U.S. Department of Energy's Office of Industrial Technologies under DOE contract no. DE-FG02-90CE40936, and by ABB/Combustion Engineering, Ahlstrom Machinery, and Kvaerner Pulping.

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