AN ABSTRACT OF THE THESIS OF


Abstract approved: Redacted for privacy

W. James Frederick

Combustion properties of kraft black liquor solids were studied using a laminar entrained flow reactor. The tendency of black liquors to release fume (compounds containing Na⁺, K⁺, Cl⁻, SO₄²⁻, SO₃⁻, S₂O₃²⁻, and CO₃²⁻) during combustion were observed at 1000 °C. Black liquor solids with a size fraction of 63 to 100 µm were burned in a mixture of 4% O₂ and 96% N₂ at a residence time of 0.67 seconds. Combustion properties of one black liquor (liquor #3) were studied by varying the solids feed rate from 0.47 to 1.08 g/min (liquor feed rate study). Combustion properties of five North American and Finnish black liquors were studied at a target solids feed rate of 0.73 g/min (liquor to liquor study).

Black liquor fuming was observed to be a decreasing function of solids feed rate and an increasing function of excess oxygen. The appearance of char residues varied from black and porous at high solids feed rates to white and dense at low solids feed rates. Combustion may have been enhanced at low solids feed rates by
liquor swelling due to a combination of heat and mass transfer effects and limited at high solids feed rates by inter-particle and bulk gas mass transfer limitations.

For the liquor to liquor study, black liquors were observed to release fume differently. Chars produced during this study varied in appearance, indicating that the black liquors had unique combustion properties. Variations in temperature and mass transfer effects resulting from liquor swelling properties were likely responsible for the variability in liquor fuming behavior. The liquors that contained the most NaCl and had the highest anionic equivalents as CO$_3^{2-}$ (or other chemical species) produced the most fume. Sodium vaporization varied from 25.2% to 33.7%: Liquors #2 and #5 vaporized the most sodium and also had the lowest concentrations of measured anions in their char residues.

Potassium and chloride enrichment factors for the five liquors were slightly lower than those of common industrial boilers. Liquor #3 had a concentration of Cl that was (roughly) an order of magnitude higher than the other liquors studied; however, it also had the lowest chloride enrichment factor.
Liquor to Liquor Differences and the Effects of Liquor Feed Rate on the Distribution of Condensed Phase Combustion Products of Kraft Black Liquor Solids Burned in a Laminar Entrained-Flow Reactor

by

Ron Train

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Redacted for privacy
Dean of Graduate School

I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

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Ron Train, Author
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<td>Carbonate Estimates for Fumes,Chars, and Black Liquors</td>
<td>135</td>
</tr>
<tr>
<td>D.1</td>
<td>Liquor to Liquor Study Data</td>
<td>140</td>
</tr>
</tbody>
</table>
LIQUOR TO LIQUOR DIFFERENCES AND THE EFFECTS
OF LIQUOR FEED RATE ON THE DISTRIBUTION
OF CONDENSED PHASE COMBUSTION PRODUCTS OF
KRAFT BLACK LIQUOR SOLIDS BURNED IN A
LAMINAR ENTRAINED-FLOW REACTOR

CHAPTER 1

INTRODUCTION

The production of pulp and paper products has become integral to our society during the 20th century and is becoming increasingly important as demand for these types of products continues to increase. Process efficiency and machine uptime have become increasingly important in the pulp and paper industry. Reduction of raw material supplies, increased governmental regulation, competition from developing markets, and the increased environmental concerns of the general public have brought about the need for industry to utilize both clean and efficient manufacturing processes. An important step in the production of wood pulp is the recycling of pulping chemicals. The chemical recycling process requires the combustion of spent pulping liquor to eliminate the organic waste products liberated during the conversion of wood to pulp fibers. The composition of spent pulping liquor can be highly variable. Chapter 1 discusses the factors that contribute to the variability of spent pulping liquor quality and the dominant
processes and equipment used by industry to generate and recover the chemicals used therein.

1.1 Biomass Fiber Variability and Utilization

Wood fibers can vary in many ways. Their physical and chemical differences combined with handling during industrial converting processes makes them unique.

1.1.1 Wood Fibers

Cellulose fibers have been utilized for centuries as the building blocks for many products that we regard as “necessities” of the modern society. Clothing, packaging, and communications media are basic consumables necessary to any human culture. Textiles have been and continue to be produced from cotton fibers — which are predominantly comprised of essentially pure cellulose. Packaging and communications media are primarily manufactured from chemically bonded wood fibers, a material that we call paper. The ancient Egyptians made the first writing material by pasting together thin layers of papyrus stems; however, it wasn’t until 100 AD that paper (as we know it today) was produced in China (Smook, 1). Modern day papermaking processes employ techniques that reduce fiber containing materials to their basic constituents. The primary constituents of woody plant stems and grasses are fibers comprised of polysaccharides and material known as lignin.
1.1.1.1 General Characteristics of Hardwoods and Softwoods

The terms "hardwood" and "softwood" are generic terms that describe two biologically different groups of plants. Hardwoods belong to the plant subdivision angiosperm and produce a seed that is covered with ovaries (or fruit); conversely, softwoods belong to the plant subdivision gymnosperm and produce a seed that is not covered with ovaries (or is "naked"). Most hardwoods grow and shed leaves annually; whereas, their softwood counterparts typically display "evergreen" foliage that does not change with the seasons. In general, hardwoods are much more specialized than softwoods: Hardwoods contain many cells that have unique biological functions that are distributed widely on a mass basis. In contrast, softwoods contain a few cell types that are in very high concentration on a mass basis, with a number of smaller cell types that are in low concentration. Table 1.1 lists the common cell types found in hardwoods and softwoods and Figure 1.1 illustrates qualitative differences of major wood cell types. In general, softwood cells (or "fibers") are much longer than hardwood fibers: The common softwood tracheid is 3-4 mm long while that of the common hardwood is less than 1 mm in length (Haygreen, 1989). Discussion of wood fibers is often focused on longitudinal tracheids because of their simplicity and high relative concentration. Longitudinal tracheids contain multiple distinct layers of "microfibrils." The microfibrils line up at differing angles characteristic of each layer and are important in establishing the physical properties of the fiber. Figure 1.2 illustrates the
Figure 1.1 Common Cells of Hardwoods and Softwoods

Figure 1.2 Representation of Softwood Tracheid Fiber
microfibril angle variation between layers of the cell wall. Four major layers within the cell are present: They are the primary, S1, S2, and S3 layers. Fibers are bordered by the middle lamella which serves the purpose of supporting and bonding the fibers together. Each layer of the fiber cell has different chemical and mechanical properties. In addition, individual fibers may have vastly different chemical make-up which is heavily dependent upon the location of the fiber within the tree: Some examples of location differences are compression wood (wood formed on the downhill side of softwoods), tension wood (wood formed on the uphill side of hardwoods), early wood (first growth of each season), and latewood (last growth of each season).
Compression wood and tension wood are often referred to as “reaction wood.” Hardwoods and softwoods have adapted different ways to accomplish the same task. While trees grow, they experience the stimulus of a changing environment: Some examples are landslides, windstorms, and gravity. Softwoods have adapted to combat stimulus by growing very dense, lignin rich wood on the opposite side of the stem experiencing stresses called compression wood. Compression wood accomplishes the task of keeping a stem straight by “pushing” it in the desired direction. In contrast, hardwoods have adapted to accomplish the same task by growing very strong, polysaccharide rich wood on the same side of the stem experiencing stresses called tension wood. Tension wood accomplishes the task of keeping a stem straight by “pulling” it in the desired direction. The photos in Figures 1.3 and 1.4 were taken of a common hardwood (Red Oak) and a common softwood (Western Hemlock) and are provided to aid the reader in understanding characteristics unique of each wood type. A glance at the cross section of the Red Oak sample shows well defined vessel elements (appearing as voids arranged in annual rings), ray cells (appearing as thick slivers passing perpendicularly through the rings), and overall variability in structure. A similar glance at the Hemlock sample reveals a relatively simple ringed cross section dominated by longitudinal tracheids.
Figure 1.3 Red Oak Structure: (1) Cross sectional view. The light colored lines are rings of vessel elements; (2) Tangential view. The dark lines are ray cells and the diffuse gray areas are vessel elements.
Latewood Annual Rings

Figure 1.4 Western Hemlock Structure: (1) Cross sectional view. (2) Tangential view. The dark lines are latewood annual rings and the light lines are earlywood annual rings. The vast majority of visible wood is composed of tracheid fibers.
1.1.1.2 Chemical Composition of Hardwoods and Softwoods

Wood is synthesized via biosynthetic processes preceded by photosynthesis. The photosynthetic process employed by plants involves the synthesis of many organic compounds from carbon dioxide, water, and energy provided by sunlight. Plants use chlorophyll, a green pigment, to absorb light in the visible spectrum and convert the energy absorbed into a form that can be used to reduce carbon dioxide and oxidize water to carbohydrates and oxygen gas (Solomons, 1992). A simplified equation illustrating this process is:

\[
xCO_2 + yH_2O + \text{solar energy} \rightarrow C_x(H_2O)_y + xO_2
\]

The principle compounds produced during photosynthesis are monosaccharides—or simple sugars. Some monosaccharides are stored as food for plants while others are further converted to polysaccharides and phenolic compounds via plant biosynthetic mechanisms. Wood fibers are primarily composed of cellulose and hemicellulose polysaccharides: The "glue" (or lignin) that holds them together is composed of bonded aromatic alcohols commonly referred to as phenylpropane units. Figure 1.5 illustrates the dominant polysaccharides found in hardwoods and softwoods (adapted from Sjostrom, 1993). Pure cellulose, or \(\beta\)-D-glucopyranose, is a long chain, un-branched polymer with a degree of polymerization of \(~10,000\) to \(15,000\). Pure cellulose constitutes 40-45% of dry wood fibers and nearly 100% of cotton fibers. Hemicelluloses are a larger group of polysaccharides that differ from cellulose in that they are branched and have a degree of polymerization of \(~200\) (Sjostrom, 1993). Hardwoods and softwoods contain differing types of
Hardwood & Softwood Cellulose
β-D-glucopyranose
dp = 10,000 to 15,000
Constitutes 40-45% of Dry Wood

Softwood Hemicellulose
galactooligomannan
dp = 200
Constitutes 20% of Dry Wood

Softwood Hemicellulose
arabinoglucuronoxylan
dp = approx. 200
Constitutes 5-10% of Dry Wood

Hardwood Hemicellulose
glucuronoxylan
dp = approx. 200
Constitutes 15-30% of Dry Wood

Hardwood Hemicellulose
glucosannan
dp = approx. 200
Constitutes 2-5% of Dry Wood

Figure 1.5 Dominant Polysaccharides of Hardwoods and Softwoods (adapted from Sjostrom, 1993)
hemicelluloses thus making them chemically unique. Hydrogen bonding is credited for the inherent strength of bonded wood fibers. Hemicelluloses are believed to enhance the strength of bonded wood fibers in paper by bridging gaps between linear, unbranched cellulose polysaccharides, and forming additional hydrogen bonds. The primary function of cellulose and hemicelluloses is to provide physical support and bulk in the cell walls of wood.

Figure 1.6 shows the precursors of hardwood and softwood lignins (adapted from Sjostrom, 1993). Unlike cellulose and hemicelluloses, lignin is not considered a member of the carbohydrate family; however, it is considered to be a polymer. Lignin varies between wood type and specie. The precise macro-chemical structure of lignin is difficult to quantify due in part to the modification of its structure during isolation from wood. The intrinsic viscosity of isolated lignins is only 1/40th that of polysaccharides suggestive of a compact, spherical structure of dissolved lignin molecules (Sjostrom, 1993). The lignin precursors described in Figure 1.6 are bonded to one another via ether and carbon-carbon linkages. Figure 1.7 shows the structure of the lignin molecule as proposed by Adler (Adler, 1977). The lignin macro-molecule is thought to bond covalently with polysaccharides (predominantly hemicelluloses) to form a lignin-carbohydrate complex (LCC) rich with ether and ester linkages (Sjostrom, 1993).

In addition to polysaccharides and lignins, a group of organic compounds termed “wood extractives” are also found in hardwoods and softwoods. “The content of extractives is usually less than 10%, but it can vary from traces up to
Softwood Lignin Precursor
coniferyl alcohol

Hardwood Lignin Precursor
p-coumaryl alcohol

Hardwood Lignin Precursor
sinapyl alcohol

Figure 1.6 Lignin Precursors of Hardwoods and Softwoods (Sjostrom, 1993)

Figure 1.7 Softwood Lignin Molecular Segment (Adler, 1977)
40% of the dry wood weight (Sjostrom, 1993).” Extractives contribute to the decay resistance of many wood species. They are exuded from wood cells especially in the vicinity of structural damage to a tree. These compounds can be extracted from wood by organic solvents or water. Extractives are most prominent in softwoods such as southern pine species, spruces, and firs, but are also found in hardwoods. In the kraft pulping process, volatile extractives (primarily turpentine) are collected and condensed from digester relief gas products; non-volatile extractives (primarily tall oil and fatty acid soaps) are skimmed from spent pulping liquors when present in high enough concentration. Pure extractives have much higher heats of combustion than black liquor.

1.1.1.3 Wood Chips: The Byproduct of Wood Converting Operations

The vast majority of timber harvested in the United States is processed for lumber and paneling products. Due to the round nature of raw logs, a significant quantity of residual material is generated during the converting process. Table 1.2 provides a material balance for the major wood converting processes (Koch, 1976). A residual pulp chip yield of 29% to 48% is common of the major raw log converting processes. Pulp chips are the raw material used for producing tissue and paper products. The United States harvested 200 to 450 million cubic meters of wood per year from 1952 to 1985 (Haygreen, 1989). Assuming a wood density of 40 lb/ft^3 and 30% moisture content, this would correspond to a range of $9.8 \times 10^7$ to $1.62 \times 10^8$ oven dry tons of wood harvested annually during that time period.
Table 1.2 Material Balances of Lumber and Plywood Converting Processes (basis: 1 ton oven dry raw logs; Koch, 1976).

<table>
<thead>
<tr>
<th>Converting Process</th>
<th>Plywood Yield</th>
<th>Lumber Yield</th>
<th>Particle Board Yield</th>
<th>Pulp Chip Yield</th>
<th>Fuel Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood Plywood</td>
<td>45%</td>
<td>6%</td>
<td>8%</td>
<td>30%</td>
<td>12%</td>
</tr>
<tr>
<td>Softwood Lumber</td>
<td>-</td>
<td>35%</td>
<td>15%</td>
<td>29%</td>
<td>21%</td>
</tr>
<tr>
<td>Hardwood Plywood</td>
<td>30%</td>
<td>-</td>
<td>-</td>
<td>48%</td>
<td>23%</td>
</tr>
</tbody>
</table>

Given the pulp chip yield of 29% to 48% from the major raw log converting processes, there has been an historic wood chip production on the order of $10^7$ oven dry tons per year (at a minimum). With such an extraordinary mass of wood being converted to chips, a considerable amount of research has been performed to quantify wood chip characteristics: This research has shown that chip thickness is the most important quality parameter for pulpwood chips because the diffusivity of liquor in wood chips is relatively constant in all directions at temperatures encountered during pulping processes. Optimal chip thickness is about 3 mm for laboratory chips; however, the optimal thickness for chips produced from industrial processes is about 5 mm because they have many additional cracks and fissures that allow additional liquor penetration (Mimms, 25).

Chips produced from industrial processes contain a wide array of lengths and thicknesses and must be fractionated in order to ensure that a consistent raw material is supplied for pulping processes. Figure 1.8 shows a disc screening...
Figure 1.8 Disc Screen Removing Oversize Hardwood Chips

Figure 1.9 Accepted Hardwood Chips Headed for Short Term Storage
device used for fractionating chips according to chip thickness. Accepts fall through the discs where they are further screened to remove fines, and rejects are transported across the discs and rejected for (1) further slicing and re-entry to the screen process or for (2) transport to a fuel pile and burned for steam generation. Figure 1.9 illustrates accept chips ready for a chemical pulping process. Another important wood chip property is moisture. Wood moisture content varies by season. Wood moisture is high during the spring and summer growing season and low during the winter months while trees remain dormant: Chip moisture can follow an opposite trend in areas with large amounts of precipitation during winter months. Mixing chips of variable moisture content can make it difficult to maintain a constant “recipe” during subsequent pulping operations.

1.1.2 Pulping Processes – Biomass Processing for the Manufacture of Pulp

The majority of wood pulping processes in use today were discovered and developed during the 19th century. All of the processes reduce raw wood to fibers – commonly referred to as pulp. The simplest and oldest industrial methods of producing pulps are mechanical processes. Due to their limited strength potentials, mechanical pulps are often supplemented with chemical pulps or recycled fibers to make a variety of products.
1.1.2.1 Mechanical Pulping Processes

Mechanical pulping processes are “high yield” because virtually all of the raw wood that is pulped is accepted and further processed into paper. The most elementary mechanical process is the groundwood process (GW) that was developed in Germany in 1840 (Smook, 1989). In the GW process, pulpwood logs are pressed against a rotating grinding stone where mechanical action shears fibers from logs. The fibers are washed away from the grinding stone with showers and the resulting pulp slurry is further processed for papermaking. A similar, more modern process of mechanical pulping is the refiner mechanical pulp (RMP) process. In the RMP process, disc refiners are used to refine wood chips. Refining discs are set at a given clearance and wood chips are forced through the rotating disc(s). The RMP process does less damage to wood fibers and produces stronger pulp than the GW process. Many versions of the RMP process have been developed during recent years: These include thermo mechanical pulping (TMP) and chemi-thermo mechanical pulping (CTMP). In TMP, steam is used to soften wood chips prior to refining; in CTMP, steam and pulping chemicals are used to soften wood chips prior to refining. Both TMP and CTMP produce higher quality mechanical pulps because fibers separate from wood much easier with less fiber fragmentation and damage.

All of the mechanical pulping processes and variations of them produce a large amount of fiber fragments, commonly referred to as “fines.” Fines have a very large specific surface area – approximately 5 to 8 times that of wood fibers.
Fines dramatically affect pulp chemical absorption capacity, pulp drainage rate, and many paper properties. Mechanical pulps are rich with lignin compounds because they are removed only in small quantities during the pulping process. Lignin compounds affect pulp optical properties as well as chemical absorption capacity. Lignin compounds are the source of color reversion in mechanical pulps, commonly observed when a newspaper is left in direct sunlight. Mechanical pulps are used whole or in part for a number of applications — including newsprint, coated magazine paper, tissue, and corrugating medium.

1.1.2.2 Chemical Pulping Processes

Two chemical processes have found their way to the forefront of modern chemical pulping: These processes are the sulfite pulping process and the kraft pulping process.

1.1.2.2.1 The Sulfite Pulping Process

The sulfite pulping process was invented by B. Tilghman in the United States and patented in 1866. Tilghman’s process incorporated calcium hydrogen sulfite and sulfur dioxide as reagents in a pressurized system. The process was used extensively until the 1950’s, when many hindrances of the process began to phase it out. First, the process is highly acidic (1.5≤pH≤ 2.3) due to the limited solubility of calcium. Second, the solubility of calcium bisulfite is inversely
proportional to temperature – so that as temperature increases, active cooking chemical concentration decreases as calcium sulfite precipitates. Third, calcium sulfate is formed during the chemical recovery process which cannot be converted back to a useful form due to temperature limitations of the associated processes (Inguber, 8).

Historically, spent sulfite pulping liquor produced from this process was discharged to the environment with little additional processing because of the readily available pulping reagents and the lack of recoverability of the spent liquor. In addition, the retention of sulfur dioxide in liquor solutions was difficult and created an odorous obstacle. For obvious reasons, this process is much less prominent than it once was; moreover, further developments in sulfite pulping have replaced the calcium base with other bases. Ammonium hydroxide was used as a base for the acid sulfite process but lost favor due to the toxicity and hazards associated with handling ammonia gas. The bases in current use are magnesium and sodium.

In general, bisulfites of the bases are formed in solution when salts of the bases are reacted with sulfurous acid (ie. Ca(HSO3)2, Mg(HSO3)2, NaHSO3, or NH4HSO3). Sulfite pulping liquors contain free sulfurous acid (H2SO3) and combined sulfurous acid (HSO3−) as the bisulfite ion. The following equilibria are present in sulfite cooking liquors:

*Equation 1.2* \[ SO_2 + H_2O \leftrightarrow H_2SO_3 (SO_2 \cdot H_2O) \]

*Equation 1.3* \[ H_2SO_3 \leftrightarrow H^+ + HSO_3^- \]
Equation 1.4 \[ HSO_3^- \leftrightarrow H^+ + SO_3^{2-} \]

Equation 1.5 \[ K_1 = \frac{[H^+][HSO_3^-]}{[SO_3^-]+[H_2SO_3]} \]

Equation 1.6 \[ K_2 = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} \]

Equation 1.7 \[ pK_1 = pH + \log \left( \frac{[HSO_3^-]}{([SO_3^-]+[H_2SO_3])} \right) \]

Equation 1.8 \[ pK_2 = pH + \log \left( \frac{[SO_3^{2-}]}{[SO_3^-]} \right) \]

The equilibrium chemical concentrations are obviously dependent upon the pH of the liquor solution. The data of Sjostrom et al (1962) show that the concentration of hydrogen sulfite ion peaks at 100% (molar basis) at pH = 4: above and below this value, the concentration of free sulfur dioxide and sulfite ions increases (at the reported experimental conditions).

Delignification occurs during acid sulfite pulping when the bisulfite ion acts as a nucleophile and attacks the α-carbon of the propane side chain of a phenylpropane group to replace ether or hydroxyl functional groups (Sjostrom, 1993). The subsequent lignosulfonic acid forms a salt in the presence of the base (calcium, magnesium, ammonium, or sodium) and becomes more soluble. Hydrolysis reactions cleave sulfonated lignin groups and complete the sulfite delignification mechanism.

The sodium process will be the focus of further discussion due to its widespread use and its incorporation with hybridized kraft chemical recovery.
processes. Sodium is soluble over essentially the entire pH range and therefore lends itself as a base for a number of sulfite pulping processes. A common sodium sulfite cooking process used for the manufacture of hardwood pulp for corrugating medium furnish is the neutral sulfite semi-chemical (NSSC) process. The advantage of the NSSC process is that the spent pulping liquor can be recovered as a mixture of Kraft and NSSC liquor with conventional chemical recovery equipment and methods. Many mills that utilize the Kraft/NSSC process use sodium sulfite and avoid the process of manufacturing the cooking reagent. Sodium sulfite is mixed with sodium carbonate (soda ash) and in some cases green liquor to create a mildly basic buffer solution: This is necessary due to the high number of acetyl groups liberated from hardwood hemicelluloses during the NSSC pulping process – as much as 3-5% of dry wood (Ingruber, 1985). Acetyl groups hydrolyze to form acetic acid and therefore act to neutralize the pulping liquor. In NSSC pulping, the principle reagent is the sulfite anion (SO$_3^{2-}$) which dissociates from sodium sulfite in solution. The sulfite anion is the nucleophile responsible for attacking phenolic lignin compounds, sulfonating them, and dissociating them.

The primary focus during the NSSC pulping process is to soften wood chips enough to allow fibers to be removed from chips with minimal damage during refining. Figure 1.10 illustrates an NSSC process commonly used in industry and Figure 1.11 shows typical NSSC industrial equipment. Wood chips are screened and washed to remove bark fragments. They are then pre-heated in the steaming vessel to aid chemical penetration and remove air. The chips are screw fed to the
Figure 1.10 Continuous NSSC Pulping Process
Figure 1.11 NSSC Pulping Equipment: (1) & (2) disc screens; (3) impregnator; (4) bottom end of a continuous digester; (5) defibrator refiner; (6) refiner plates – note radial bars.
impregnator. A level of sulfite liquor is maintained in the impregnator and the chips absorb liquor upon contact.

The liquor charge is typically 8 to 14% sodium sulfite and 2.5% to 5% soda ash (or equivalent green liquor buffer) calculated based on oven dry wood. After a short residence time in the impregnator (1.5 minutes), the chips are transferred to the continuous digester where they are cooked in plug flow for 15 to 35 minutes depending on pulp grade and production rate. The temperature can reach 210°C during the cooking process. Liquor to wood ratio is typically low (~1.5:1) because the pulping essentially takes place in the “vapor phase.”

The chips are conveyed out of the digester to a refiner where they are refined. The refiner plates are designed with staggered bars (see Figure 1.11-6) that defiber and grind the softened wood chips. Power requirements are significantly reduced by steaming immediately prior to the refiner (see Figure 1.11-5); however, they remain very high at 10 to 30 hp-day/ton. Following refining, the fiber is blown into a storage tank and washed with displacement washers.

The end products of the washing stage are NSSC pulp produced at a yield of 75% to 85% and spent NSSC cooking liquor that contains an approximate residual sulfite content of 5 to 10 g/L. Figure 1.12 shows two examples of corrugating medium (prior to corrugation) produced from NSSC and green liquor semi-chemical processes, respectively. Sample 1 in Figure 1.12 contains 60% NSSC hardwood pulp and 40% post consumer recycled fibers. Sample 2 in Figure 1.12 contains 60% green liquor semi-chemical hardwood pulp and 40% post
Figure 1.12 Samples of Semichemical and Kraft Papers: (1) NSSC corrugating medium; (2) green liquor corrugating medium; (3) kraft linerboard
consumer recycled fibers. Spent NSSC pulping liquor is concentrated and incinerated in some mills, while others (if the option exists) mix it with kraft black liquor, concentrate it, and burn it for chemical recovery and steam generation.

1.1.2.2.2 The Kraft Pulping Process

The kraft chemical pulping process was developed in Germany by Carl Dahl in 1884 and was a significant improvement over the soda pulping process used at that time. The kinetics of the kraft process are more favorable than the kinetics of soda process and the resulting pulp is generally much stronger (kraft is a German word meaning “strong”). Kraft pulping liquor, or white liquor, is composed of a mixture of sodium hydroxide and sodium sulfide, as well as other inactive compounds in low concentration. White liquor typically has pH=13.5-14. The principle nucleophiles responsible for the pulping reactions are the hydroxyl ion and the hydrogen sulfide ion. The following chemical equilibria are present in white liquor:

\[
\text{Equation 1.9} \quad S^{2-} + H_2O \leftrightarrow SH^- + OH^- \\
\text{Equation 1.10} \quad SH^- + H_2O \leftrightarrow H_2S + OH^- \\
\text{Equation 1.11} \quad K_1 = \frac{[SH^-][OH^-]}{[S^{2-}]} \\
\text{Equation 1.12} \quad K_2 = \frac{[H_2S][OH^-]}{[HS^-]}
\]
The equilibrium constants have been shown to be $K_1 \sim 10$ and $K_2 \sim 10^7$; therefore, the concentration of the hydrogen sulfide ion prevails in white liquor (Sjostrom, 1993). As pH is lowered, the concentration of hydrogen sulfide becomes significant at about pH=8 and must be considered when dealing with kraft white liquor, green liquor, or spent black liquor due to the toxicity of hydrogen sulfide gas. Fortunately, pulping and recovery process liquor pH rarely falls below pH=10 in modern pulping and recovery processes. Many expressions have been developed to quantify the properties of white liquor for kraft pulping: These expressions are customarily calculated based on equivalents of sodium oxide (Na$_2$O). Total alkali, active alkali, and effective alkali are usually expressed in units of lb/ft$^3$ when used to describe raw white liquor properties; however, active alkali and effective alkali are usually expressed as a chemical “charge” percentage of dry wood.

**Equation 1.13**

\[ \text{Total Alkali} = \text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3 \]

**Equation 1.14**

\[ \text{Active Alkali} = 100\% \times \left( \frac{\text{NaOH} + \text{Na}_2\text{S}}{\text{dry wood}} \right) \]

**Equation 1.15**

\[ \text{Effective Alkali} = 100\% \times \left( \frac{\text{NaOH} + 0.5 \times \text{Na}_2\text{S}}{\text{dry wood}} \right) \]

when discussed as parameters for kraft pulping. In addition to the aforementioned expressions, the sulfidity of the pulping liquor is an important quantity:

**Equation 1.16**

\[ \text{Sulfidity} = 100\% \times \left( \frac{\text{Na}_2\text{S}}{\text{Na}_2\text{S} + \text{NaOH}} \right) \]

The general consensus of the industry is that maximizing sulfidity is a favorable practice due to benefits in pulp strength and yield; however, high sulfidity can
contribute to elevated sulfur emissions and special recovery boiler design requirements.

Conventional kraft pulping is carried out in the liquid phase. As such, the liquor to wood ratio is an important quantity for establishing chemical concentrations during the cooking process. The liquor to wood ratio does not include the quantity of liquid in wood chips and consequently may lead to error in establishing uniform chemical concentrations during cooking due to seasonal variations of chip moisture: This error can be eliminated by using a “liquid to wood” ratio that includes chip moisture. Typical industrial values for the

\[
\text{Equation 1.17 Liquid : Wood} = \frac{\text{white liquor} + \text{black liquor} + \text{chip moisture}}{\text{dry wood}}
\]

quantities mentioned in equations 1.13 through 1.17 are summarized in Table 1.3. The values vary according to grade requirements of the desired pulp.

Table 1.3. Kraft Pulping Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Typical Range</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Alkali</td>
<td>~7</td>
<td>lb/ft^3</td>
</tr>
<tr>
<td>Active Alkali</td>
<td>13 – 18</td>
<td>% of dry wood (as Na_2O)</td>
</tr>
<tr>
<td>Effective Alkali</td>
<td>11 – 16</td>
<td>% of dry wood (as Na_2O)</td>
</tr>
<tr>
<td>Sulfidity</td>
<td>21-33</td>
<td>%</td>
</tr>
<tr>
<td>Liquid:Wood</td>
<td>2-5</td>
<td>mass ratio</td>
</tr>
<tr>
<td>Pulp Yield</td>
<td>40-60</td>
<td>%</td>
</tr>
<tr>
<td>H-factor</td>
<td>500-2000</td>
<td>reported dimensionless</td>
</tr>
</tbody>
</table>
Due to the number of chemical compounds present and the complexity of the reactions that occur during kraft pulping, a quantity termed "H-factor" has been developed to provide a basis for evaluating the delignification of wood during the pulping process (Vroom, 1957). The delignification process can be described using pseudo first order kinetics and the rate constant can be calculated using the Arrhenius equation:

\[ \frac{dL}{dt} = kL \]  

\[ \ln k = \ln A - \frac{E_a}{RT} \]  

The H-factor is the time integral of the relative reaction rate:

\[ H_{factor} = \int_{t_i}^{t_f} \exp\left(\ln A - \frac{E_a}{RT}\right) dt \]

It follows from equation 1.20 that the H-factor is equivalent to the area under the curve of the relative reaction rate of delignification plotted as a function of time. Since temperature \( T \) is a function of time \( t \), the integral in equation 1.20 is evaluated numerically. A reference of H-factor = 1 is assigned at 100°C. In theory, kraft cooks with identical alkali charge, liquor sulfidity, liquid to wood ratio, and H-factor should produce pulp with identical properties. In practice, other correction factors may be necessary to account for variations in pulping parameters and chip quality.

The delignification mechanism of kraft pulping is similar to that of sulfite pulping in that ether linkages within lignin are attacked and resulting structures are
dissolved in the pulping liquor as sodium phenolate compounds. The process is accelerated due to the presence of the hydrogen sulfide ion and its high nucleophilicity relative to that of the hydroxyl ion. The degree of delignification of wood pulp (kraft or otherwise) is determined by titration and is often reported as the kappa number. In the kappa test, a sample of screened and disintegrated pulp is reacted with 0.1000 \( N \) KMnO\(_4\) and 1.0 \( N \) H\(_2\)SO\(_4\) for ten minutes and quenched with 1.0 \( N \) KI. The kappa number is the volume (in mL) of 0.1 \( N \) KMnO\(_4\) consumed by lignin in the pulp sample during the ten minute reaction time corrected to 50% consumption. The concentration of lignin in the original pulp sample (for kraft pulp) has been reported to be related to kappa number according to equation 1.21 (Mimms, 1993).

\[ \text{Equation 1.21} \quad \text{Lignin (\%) = 0.147} \times \text{kappa number} \]

The concentration of lignin in wood pulp establishes pulp quality and is important for subsequent bleaching and/or papermaking operations. The make-up of the spent pulping liquor (or black liquor) is dependent on pulp mill operations: Variations in the organic composition of pulping liquor can be introduced by inadequate process control in the pulp mill. These variations are commonly scrutinized due to their adverse impact on pulp properties; however, they also cause variability in black liquor properties that can have an impact on chemical recovery operations and efficiencies.

Kraft pulping equipment is similar to sulfite pulping equipment. Figure 1.13 provides a schematic of the kraft batch pulping process. The pulping process
Figure 1.13 Batch Kraft Pulping Process
can be carried out with a continuous digester (as in Figure 1.11-4) or batch digesters (as in Figure 1.14-3). In the batch process, wood chips are screened and conveyed to digesters. The digesters are typically filled with chips and pulping liquor simultaneously to improve chip packing. Steam can also be added during the digester filling stage to remove air. Once the digester is filled with chips, calculations are performed to determine the final liquor content required to meet pulping parameters for the grade of pulp being produced. Some mills use data from previous cooks to extrapolate for the current cook to speed up the process. Liquor is added and the digester is capped off.

The cook begins when steam brings the digester temperature up to 100°C. The maximum temperature during the cooking process is about 180°C. Delignification during kraft pulping occurs in three phases. The initial phase (I) is characterized by rapid lignin removal; the bulk delignification phase (II) is characterized by the first order rate in equation 1.19; and the residual delignification phase (III) is characterized by slow lignin removal coupled with moderate cellulose deterioration. The slow removal of lignin during stage III is thought to occur due to lignin condensation reactions in which carbon-carbon bonds are formed between dissolved lignin and lignin bonded to polysaccharides (Sjostrom, 1993). A significant portion of hemicellulose is removed during stages (I) and (II).

The kraft cook ends when the desired H-factor is reached: The blow valve on the digester is opened and pulp is blown into a blow tank where it impinges on a
Figure 1.14 Kraft Pulping Equipment: (1) softwood chips in short term storage; (2) softwood chips on a conveyor headed for the batch digesters – screened chips vary widely in length but have a uniform thickness profile; (3) batch digesters; (4) target plate at the top of a blow tank; (5) line of kraft pulp displacement washers; (6) freshly washed kraft pulp headed for the paper mill.
target plate (Figure 1.14-4). As the hot pulp and liquor are blown into the tank at near atmospheric conditions, hot gases containing steam, non-condensable gases (NCG’s), wood acids, and methanol are sent to the blow heat recovery system. Most mills warm up water with flash steam generated during the pulp blowing process. NCG’s are recovered and incinerated at high temperature.

Pulp is removed from the blow tank and defibered with fibrilizers and hot stock refiners. Following refining, the pulp is screened and washed (Figure 1.14-5). Screen rejects are commonly re-introduced to the blow tank following a reject-refining step. Washed pulp (Figure 1.14-6) is stored in high density storage tanks. Sample 3 in Figure 1.12 is linerboard (commonly the outside layer of a corrugated paper box) and contains 75% softwood kraft pulp and a 25% mixture of pre- and post-consumer recycled fibers. A clear difference in paper properties can be observed between the samples in Figure 1.12.

1.2 Recovery of Kraft Chemicals and Energy Utilization

The kraft process is unique among wood pulping processes in that process chemicals may be recovered and reused. Black liquor is processed, burned, and the resulting smelt is dissolved in water and reacted with calcium hydroxide to complete the kraft chemical recovery cycle.
1.2.1 Black Liquor

Spent kraft pulping liquor serves as the fuel for a unique type of boiler called the chemical recovery boiler. Most fuels (oil, natural gas, bark, etc.) contain a small amount of inorganic material relative to their organic composition; however, black liquor differs from common fuels.

1.2.1.1 Black Liquor Properties

Concentrated black liquor may contain upwards of 30% inorganic materials, mostly sodium and sulfur: For this reason, chemical recovery boilers have special

Table 1.4 Chemical species and elemental compositions of kraft black liquors from North American wood species for virgin black liquors (i.e. prior to mix tank) (Frederick, 1997)

<table>
<thead>
<tr>
<th>Chemical species in kraft black liquor</th>
<th>Typical Range (mass %)</th>
<th>Elemental composition of kraft black liquor</th>
<th>Typical Range (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali lignin</td>
<td>30-45%</td>
<td>Carbon</td>
<td>34-39%</td>
</tr>
<tr>
<td>Hydroxy acids</td>
<td>25-35%</td>
<td>Hydrogen</td>
<td>3-5%</td>
</tr>
<tr>
<td>Extractives</td>
<td>3-5%</td>
<td>Oxygen</td>
<td>33-38%</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>5%</td>
<td>Sodium</td>
<td>17-25%</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>3%</td>
<td>Sulfur</td>
<td>3-7%</td>
</tr>
<tr>
<td>Methanol</td>
<td>1%</td>
<td>Potassium</td>
<td>0.1-2%</td>
</tr>
<tr>
<td>Sulfur</td>
<td>3-5%</td>
<td>Chloride</td>
<td>0.2-2%</td>
</tr>
<tr>
<td>Sodium</td>
<td>15-20%</td>
<td>Nitrogen</td>
<td>0.04-0.2%</td>
</tr>
</tbody>
</table>
design features for dealing with the unique challenges presented by black liquor fuel. A typical composition of kraft black liquor is provided in Table 1.4 (Frederick, 1997). Black liquor properties are very dependent on solids concentration, temperature, and, in some cases, residual active alkali content: For these reasons, the majority of physical and chemical property data available for black liquor has been generated empirically. Functional relationships of selected

Table 1.5 Functional Relationships of Selected Black Liquor Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Functional Relationship</th>
<th>Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>$S_{GBL} = 0.9982 + 0.006(S) - 0.0003(T)$</td>
<td>$S =$ BL solids (%)</td>
</tr>
<tr>
<td>Boiling Point Rise</td>
<td>$\Delta T_{BPR} = \Delta T_{BPR.50}(S)/(1-S)$</td>
<td>$S =$ BL solids (%)</td>
</tr>
<tr>
<td></td>
<td>$\Delta T_{BPR.50} = BPR @ S=50%$</td>
<td>$\Delta T_{BPR.50}(\pm20%) \sim 24.3^\circ F$</td>
</tr>
<tr>
<td></td>
<td>$\Delta T_{BPR.50} = (\pm20%) \sim 24.3^\circ F$</td>
<td></td>
</tr>
<tr>
<td>Specific Heat, $C_p$</td>
<td>$C_p = 1.0 - (1- C_{p,s})S$</td>
<td>$S =$ BL solids (%)</td>
</tr>
<tr>
<td>(Btu/lbm °F)</td>
<td></td>
<td>$C_{p,s} =$ specific heat of solids $\sim 0.50$</td>
</tr>
<tr>
<td>Thermal Conductivity, $k$</td>
<td>$k = 0.832 * 10^{-3}(T) - 1.93 * 10^{-3}(S) + 0.321$</td>
<td>$S =$ BL solids (%)</td>
</tr>
<tr>
<td>(Btu/(hr ft °F))</td>
<td></td>
<td>$T =$ temperature (°F)</td>
</tr>
<tr>
<td>Viscosity, low shear</td>
<td>$\log(\mu_b/\mu_w)=(S^<em>/T)/((0.679-0.656</em>(S^*/T))$</td>
<td>$ST^*/T =$ reduced solids</td>
</tr>
<tr>
<td>(Pa-s)</td>
<td>Where $\mu_w = 1/(36.6T-10090)$</td>
<td>where $T^* = 373K =$</td>
</tr>
<tr>
<td></td>
<td>$\pm 1%$ for $333^\circ K \leq T \leq 473^\circ K$</td>
<td>reference temperature</td>
</tr>
<tr>
<td>Net Heating Value</td>
<td>$\sim 5201$</td>
<td>average value- highly</td>
</tr>
<tr>
<td>(Btu/lb BLS)</td>
<td></td>
<td>dependent on process</td>
</tr>
<tr>
<td></td>
<td></td>
<td>variables and liquor</td>
</tr>
<tr>
<td></td>
<td></td>
<td>source</td>
</tr>
</tbody>
</table>
black liquor properties are provided in Table 1.5 (Adams*, 1997; Frederick*, 1997; Green*, 1991).

When compared with other organic fuels, black liquor is relatively low grade: It has about 50% of the heating value of clean coal and 25% of the heating value of natural gas or fuel oil (Weston, 1992). The behavior of black liquor is difficult to predict – as is evidence by the accuracy of the correlation given for viscosity in Table 1.5: This is due to the variable, complex organic and inorganic composition of black liquor. Residual active alkali (RAA) has been shown to reduce liquor viscosity as it increases: An increase of 1% in the RAA content of black liquor solids has been shown to reduce the viscosity of black liquor at 70% solids content by as much as 50% (Milanova, 1990). In addition, experiments have shown that heat treatment of black liquor above 140°C can reduce viscosity significantly by degrading lignin and carbohydrate compounds within the liquor (Ryham, 1989).

1.2.1.2 Evaporation and Concentration of Black Liquor

Black liquor is provided from the pulp mill at approximately 12-17% solids – depending on pulp washing efficiency. In order to realize the benefits of black liquor as a fuel, it must be concentrated up to 65-70% dry solids concentration. There are many ways to accomplish this task: One of them is to use multi-effect evaporators. With multi-effect evaporators, steam flows counter current with black liquor. A typical arrangement may contain up to six effects and be capable of
evaporating 5 pounds of water per pound of supply steam. Black liquor enters the 5th and 6th effects under vacuum. The evaporators are designed like shell and tube heat exchangers with steam condensing on the tubes and heating the black liquor to its respective boiling point. The vapor generated from boiling the black liquor in one effect is transported to the next effect and condensed on the tubes within. As the liquor flows from effect to effect, it experiences a boiling point rise due to the increase of the concentration of dissolved material in the liquor.

Efficient operation of multi-effect evaporators requires that the heat transfer surfaces within remain clean. Scale build-up on the liquor side heat transfer surfaces of multi-effect evaporators can be a major problem. Scale can be formed when complexes of calcium ion with lignin fragments decompose and release calcium ion, which reacts with carbonate ion which is present in the black liquor (Frederick, 1981). Scale can also be formed when the solubility limit of sodium sulfate and sodium carbonate are reached during the evaporation process (Frederick, 1981; Golike et al., 2000). Multi-effect evaporators require frequent hydro-blasting to maintain their heat transfer efficiency.

A newer method of evaporating liquor is applied using a falling film evaporator. The pressures and temperatures are typically much lower and help minimize scale caused by reverse solubility of calcium and sulfur compounds (Green, 1991). Figure 1.15 illustrates a falling film evaporator that uses recovered blow heat to evaporate water from black liquor.
Figure 1.15 A Modern Falling Film Blow Heat Evaporator

Figure 1.16 A Direct Contact Evaporator (Cascade Type), chemical ash mix tank in foreground
Regardless of the method used, evaporated liquor generally contains 50% dry solids and requires further concentration prior to firing. At solids concentrations above 50%, the solubility limit of many dissolved compounds in the liquor is exceeded and equipment must be designed with this taken into account. For many years, direct contact evaporators (DCE) have been standard equipment on chemical recovery boilers. The general concept is to pass hot flue gases discharged from the economizer of the boiler through a device that maximizes heat transfer surface area of liquid black liquor. Two such devices currently in use are the cascade evaporator and the cyclone evaporator (refer to Figure 1.16). The hot flue gases pick up moisture from the liquor as they pass by. Unfortunately, the flue gases also pick up unwanted reduced sulfur compounds; thus necessitating black liquor oxidation prior to direct contact evaporation. The process of oxidizing black liquor usually is accomplished by blowing air through hot black liquor in a way that maximizes mass transfer. Oxidation is an exothermic process that converts sulfides to thiosulfates and partially decomposes polysaccharide and lignin compounds; therefore, a portion of the energy in the black liquor that could be utilized in the recovery boiler is irreversibly lost. Despite the oxidation of the majority of the hydrogen sulfide present in the black liquor to sodium thiosulfate, acids in the flue gases (CO₂, SO₂, HCl) lower the pH at the gas-liquor interface thereby allowing residual sulfide to form hydrogen sulfide gas and contribute to TRS emissions (Iisa, 1997). Liquor leaving the direct contact evaporator can have a solids content up to 68%. Some mills mix ash from the sootblowers and
precipitator with black liquor in the DCE. Most mills that do not have a DCE utilize a mix tank to add make-up chemicals (predominantly saltcake — and possibly other chemicals rich in sodium and sulfur) and ash from the ash hoppers and precipitators. Newer chemical recovery units utilize specially designed concentrators that reduce scale deposition by operating at high liquor recirculation rates.

1.2.1.3 Combustion Mechanism of Kraft Black Liquor

Many solid fuels that contain moisture progress through 3 distinct phases as they burn: These phases are drying, devolatilization, and char combustion. The process can be observed when a block of wood is burned in an open fire. As the temperature of the wood block increases, water vapor is released from the wood surface (drying) until a critical temperature is reached at which ignition of volatile organic material near the wood surface takes place (devolatilization). The process continues to progress as oxygen diffuses into the burning wood matrix, gasified carbon diffuses out, and burning occurs in the flame that envelops the solid wood (char burning). The heterogeneous process continues until all of the carbon in the char matrix is gasified and burned or until the process is interrupted. The remaining inorganic material collapses from the original wood matrix and settles out as ash. Kraft black liquor combustion progresses through similar phases as common solid fuels; however, the elevated levels of inorganic materials and
I. Drying

II. Devolatilization

III. Char Burning

IV. Smelt Coalescence and Reactions

Figure 1.17 Combustion Mechanism of Kraft Black Liquor Droplet
organic variabilities in kraft black liquor have a measurable impact on its combustion behavior.

Figure 1.17 depicts the combustion mechanism of a kraft black liquor droplet. During stage (I), heat is transferred to the black liquor droplet by radiation and convection. The temperature within the particle rises as heat conducts thorough it and quickly evaporates water. The release of water vapor can create somewhat violent surface activity and release very small black liquor particles (1-100 μm), or “ejecta” (Verrill, 1994). These particles rapidly progress through the combustion process and can be easily transported with flue gases in a boiler. Black liquor begins to swell during the drying stage (Hupa, 1987).

The devolatilization stage (II) begins with the ignition of gasification products at the surface of the liquor drop. Swelling that began during the drying stage continues at a rapid rate until a maximum swollen volume is reached: Volume expansions by a factor of 20 to 50 are common during combustion at typical recovery boiler conditions (Frederick, 1997). Large variations in swelling behavior between different black liquors burned at identical conditions have been observed (Frederick et al, 1991). Lignin content, pH, dead load chemical content, and tall oil concentration have been shown to effect the swelling properties of black liquor; however, liquor to liquor variations in swelling have not been explained in terms of liquor composition and properties (Frederick, 1997). Swelling is caused by the expansion of pyrolysis and combustion products within the liquor particle. Swelling causes the surface area of the burning liquor particle to increase.
dramatically; however, thermal conductivity within the liquor particle is decreased as a result. Research has indicated that steep temperature gradients exist within swollen black liquor droplets (Frederick, 1990).

The devolatilization stage is characterized by thermal breakdown of organics within black liquor and is often described analogously with pyrolysis; however, strictly speaking, pyrolysis occurs in an inert environment whereas devolatilization can occur under oxidizing, reducing, or inert conditions. During devolatilization, organics are first released as tar and then quickly converted to CO, CO₂, H₂O, NH₃, NO, light hydrocarbons, H₂S, and other reduced sulfur compounds (Frederick, 1997). Combustion experiments with black liquor solids and liquid black liquor (37.1% dry solids) in a quartz tube reactor at 1100°C and 95% He / 5% O₂ have shown that a large amount of SO₂ gas is released during the devolatilization stage (Dayton & Frederick, 1996). Fragmentation of the burning black liquor can take place during the devolatilization stage and contribute to the generation of small liquor particles (1-100 μm).

The char burning stage (III) begins when the volatile gases emitted by the liquor particle are consumed and the flame at the particle surface disappears. Experiments by Dayton and Frederick have shown that the majority of the inorganic fume released during black liquor combustion is generated during char burning. For black liquor solids and droplet combustion, sodium, potassium, and chlorine were predominantly released during char burning. The majority of the sodium measured was as NaCl; therefore, the authors concluded that NaCl
dominates in the absence of SO$_2$ (Dayton & Frederick, 1996). Under normal recovery boiler conditions, SO$_2$ is captured by sodium in the presence of oxygen and water in the gas phase (Boonsongsup et al., 1997) converting the NaOH, Na$_2$CO$_3$ and NaCl in sub-micron aerosol particles to Na$_2$SO$_4$: The fine particles collect. During the char burning stage, O$_2$, CO$_2$, and H$_2$O diffuse into the char matrix and gasify carbon: CO, H$_2$, and CO$_2$ are the primary products of the char burning process. The inorganic material present in char acts as a catalyst during char combustion. Na$_2$SO$_4$ and Na$_2$CO$_3$ are reduced by solid carbon to form Na$_2$S and, to a lesser extent, Na$_2$(v). Fragmentation and shedding can take place during char combustion; however, the majority of inorganics released during char burning that contribute to sub-micron fume formation on recovery boiler heat transfer surfaces are Na, NaCl, and KCl.

The fourth and final stage of black liquor combustion is the smelt coalescence and reactions stage (IV) and is characterized by the collapse of the char particle to a “bead” of molten smelt. The molten smelt contains Na$_2$S, Na$_2$CO$_3$, iron and other trace inorganic materials, and un-combusted carbon: The Na$_2$S in smelt can react violently with oxygen to form sodium sulfate. The oxidation of Na$_2$S can produce a “sparking” condition at the smelt surface. The combustion of a droplet of black liquor fired into a recovery boiler follows a similar path as described in Figure 1.17; however, there is a larger degree of stage overlap and the combustion process is more diffuse due to the random droplet size and the composition of the gases within the boiler.
1.2.2 The Kraft Chemical Recovery Boiler

The first prototype of the kraft chemical recovery boiler was designed by G.H. Tomlinson and constructed in collaboration with Babcock & Wilcox (B&W) in 1934 (Smook, 1989). The Tomlinson design has been used extensively during the 20th century. Figure 1.18 shows a simplified schematic of a chemical recovery boiler manufactured by Combustion Engineering (C-E). Figures 1.19-1 and 1.19-2 show chemical recovery industrial equipment. The chemical recovery boiler is the heart of the kraft process and bears a large responsibility for the safe, efficient, economical, and clean operation of the mill. A brief lapse of neglect during operation can lead to a plugged boiler and expensive downtime, excessive emissions, or worse yet, a catastrophic explosion. The key functions of the chemical recovery boiler are summarized in Table 1.6. Chemical recovery boilers are designed to maximize heat transfer between the gases generated during

Table 1.6 Functions of the Kraft Recovery Boiler

<table>
<thead>
<tr>
<th>Functions of the Kraft Recovery Boiler</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduce sulfur compounds to Na₂S and convert remaining sodium to Na₂CO₃</td>
</tr>
<tr>
<td>Generate steam for power generation or other end use by fully utilizing fuel value of black liquor</td>
</tr>
<tr>
<td>Maximize run time between outages for water washes (i.e., minimize carryover and plugging)</td>
</tr>
<tr>
<td>Minimize emissions of: (1) particulate, (2) reduced sulfur compounds, (3) oxidized sulfur compounds, (4) volatile organic compounds (VOC's), (5) oxidized nitrogen compounds</td>
</tr>
</tbody>
</table>
Figure 1.18 Kraft Chemical Recovery Boiler System (Typical C-E Design)
Figure 1.19-1 Kraft Chemical Recovery Equipment (I) (Combustion Engineering unit featured): (1) two chemical recovery boilers with green liquor clarifiers in foreground; (2) smelt dissolving tank; (3) molten smelt pouring from a smelt spout; (4) primary air ports; (5) black liquor firing gun; (6) secondary air ports.
Figure 1.19-2 Kraft Chemical Recovery Equipment (II) (Combustion Engineering unit featured): (1) ash hoppers; (2) mud drum; (3) sootblowers at the generating bank; (4) upper portion of superheater (left), generating bank & steam drum (center), and economizer (right); (5) economizer at the penthouse of the boiler; (6) electrostatic precipitator.
combustion and water flowing through tubes within the boiler. In many ways, a chemical recovery boiler resembles a counter flow heat exchanger. The walls, or "water walls", of the boiler are designed with tubes traveling vertically through them, and the floor is designed in a similar way. Water enters the boiler in the economizer (Figure 1.19-2-5) where it is heated by flue gas as it exits the boiler. It then travels to the steam drum (Figure 1.19-2-4) of the boiler bank where it flows down to the mud drum and is distributed to the tubes in the bottom of the boiler. A portion of the water may be diverted to the screen tubes of the boiler where it flows upward and vaporizes prior to discharge to the steam drum. As the water is heated, it boils and vaporizes as it travels through the water wall tubes and is discharged to the steam drum of the boiler bank. The final path of the steam prior to exiting the boiler is through the superheater unit (Figure 1.19-2-4) where hot combustion products pass by initially saturated steam to heat it to the degree of superheat required for subsequent mill processes.

Some chemical recovery boilers are designed to operate in the 1000-1500 psig throttle pressure range for power generation while others operate in the 350 psig range for process steam production. A Combustion Engineering unit can be capable of firing $1.1 \times 10^6$ lb of black liquor solids per day and generating $1.2 \times 10^5$ lb of steam per hour at 350 psi and 700°F. The combustion of black liquor is a complex process of drying, devolatilization, char burning, and smelt coalescence (Frederick, 1997). Black liquor is fired above the primary wind box (see Figure 1.19-1-5) where it dries in free flight as it falls to the char bed at the bottom of the
boiler. Firing rate, droplet size, and air flows are extremely important because they determine the extent of “carryover” of liquor particles leaving with the flue gas and have a direct impact on the deposition of inorganics on the heat transfer surfaces downstream.

There are three distinct reaction zones within the recovery boiler and air is supplied to each zone accordingly to control the rate of combustion and chemical conversion. The reducing zone (zone 1) is at the char bed in the bottom of the furnace. Primary air is supplied to the char bed to provide enough oxygen to gasify carbon compounds in the char bed while minimizing oxidation of sulfur compounds. The drying zone (zone 2) of the boiler is located in the vicinity of the liquor guns. Some recovery boilers are designed to deliver a portion of air below the liquor guns (secondary) and above the liquor guns (tertiary). In any case, the drying zone is basically a pyrolysis zone where carbon containing products are emitted from the drying/devolatilizing liquor. In boilers that are not equipped with tertiary air, secondary air is supplied above the liquor guns to provide oxidizing conditions (zone 3) for completing the combustion of the pyrolysis and gasification products from the lower furnace. Mixing is important for complete combustion to be realized in zone 3. The chemical reactions of major significance that occur in the three zones are summarized in Table 1.7. By the time the liquor has reached the char bed, most of the volatile compounds are absent and the liquor takes the form of a porous char containing carbon and inorganics. As carbon in the char is oxidized, the heat liberated keeps the smelt bed in a molten state (see Figure
The temperatures encountered in the smelt bed (~1000°C) are sufficient to vaporize sodium through carbonate reduction and are also sufficient to vaporize

Table 1.7 Dominant Chemical Reactions within Chemical Recovery Boiler Zones (adapted from Grace & Frederick, 1997; Smook, 1989)

<table>
<thead>
<tr>
<th>Zone</th>
<th>Dominant Chemical Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Reducing (char bed)</td>
<td>organics + energy → pyrolysis products</td>
</tr>
<tr>
<td></td>
<td>$C + O_2 \rightarrow 2CO$</td>
</tr>
<tr>
<td></td>
<td>$CO + 0.5O_2 \rightarrow CO_2$</td>
</tr>
<tr>
<td></td>
<td>$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$</td>
</tr>
<tr>
<td></td>
<td>$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO$</td>
</tr>
<tr>
<td></td>
<td>$Na_2S + 2O_2 \rightarrow Na_2SO_4$</td>
</tr>
<tr>
<td></td>
<td>$Na_2SO_4 + C \rightarrow Na_2O + CO + SO_2$</td>
</tr>
<tr>
<td></td>
<td>$C + H_2O \rightarrow CO + H_2$</td>
</tr>
<tr>
<td></td>
<td>$Na_2S + H_2O \rightarrow Na_2O + H_2S$</td>
</tr>
<tr>
<td></td>
<td>$2C + Na_2CO_3 \rightarrow 2Na(v) + 3CO$</td>
</tr>
<tr>
<td>2 Drying (firing deck)</td>
<td>organics + energy → pyrolysis products</td>
</tr>
<tr>
<td></td>
<td>$Na_2S + CO_2 + H_2O \rightarrow Na_2CO_3 + H_2S$</td>
</tr>
<tr>
<td></td>
<td>$Na_2O + CO_2 \rightarrow Na_2CO_3$</td>
</tr>
<tr>
<td></td>
<td>$Na_2O + H_2O \rightarrow 2NaOH$</td>
</tr>
<tr>
<td>3 Oxidizing (upper furnace)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$CO + 0.5O_2 \rightarrow CO_2$</td>
</tr>
<tr>
<td></td>
<td>$H_2 + 0.5O_2 \rightarrow H_2O$</td>
</tr>
<tr>
<td></td>
<td>$H_2S + 1.5O_2 \rightarrow SO_2 + H_2O$</td>
</tr>
<tr>
<td></td>
<td>$Na_2S + 2O_2 \rightarrow Na_2SO_4$</td>
</tr>
<tr>
<td></td>
<td>$Na_2CO_3 + SO_3 \rightarrow Na_2SO_4 + CO_2$</td>
</tr>
<tr>
<td></td>
<td>$Na_2S + 1.5O_2 + CO_2 \rightarrow Na_2CO_3 + SO_2$</td>
</tr>
<tr>
<td></td>
<td>$Na_2SO_3 + 0.5O_2 \rightarrow Na_2SO_4$</td>
</tr>
</tbody>
</table>
chlorides of potassium and sodium: These vaporized alkali metals and their chlorides are important contributors to boiler fouling and are discussed in detail in Chapter 4. Smelt is decanted (C-E or Ahlstrom boilers) or poured (B&W or Kvaerner boilers) from the char bed and dispersed by shatter jets as it enters the dissolver at the ground level of the boiler. The shatter jets reduce the smelt droplet size to minimize the chances of a smelt-water explosion. The dissolved smelt contains sodium sulfide, sodium carbonate, a small amount of organic material, and other inorganic compounds dissolved from wood during the pulping process. The liquid produced in the dissolver is called green liquor and is pumped to the caustic plant for further processing (see §1.2.3).

As previously mentioned, air is supplied to the furnace through primary, secondary, and (if applicable) tertiary air ducts (Figures 1.19-1-4 and 1.19-1-6). Air is supplied to the furnace at 5-7% excess (Weston, 1992) with approximately 50%-60% as primary air and the balance roughly split between secondary and tertiary air. Steam coil air heaters are usually employed to heat the air supply as it exits the forced draft fan. The design requires that adequate air is supplied to achieve the desired carbon oxidation without adversely affecting sulfur reduction. Entrainment of particles in the upper furnace gases are minimized by supplying low velocity air at the primary wind boxes. As hot pyrolysis, gasification, and devolatilization products rise from the char bed above the firing guns, secondary air is provided at a sufficient velocity to mix the reactants thoroughly. The hot gases containing combustion products and vaporized alkali metal salts are diverted by the
nose arch in the upper furnace prior to travel through a series of heat exchange tubes. Heat is transferred to steam at the superheater. At this point, entrained particles and vaporized alkali metals begin to condense on heat transfer surfaces as sodium sulfate, sodium carbonate, potassium sulfate, potassium carbonate, sodium sulfide, potassium sulfide, sodium chloride, and potassium chloride. Sootblowers are distributed throughout the superheater, boiler bank, and economizer (see Figure 1.19-2-3). The sootblowers remove condensed deposits from the heat exchange tubes by passing steam through a rotating nozzle between tube banks. The deposits that are removed fall below to the char bed, ash hoppers, or the direct contact evaporator (if applicable). The deposits contain a mixture of condensed aerosols ("fume") and entrainment carryover with individual particles ranging in size from $10^{-1} \mu m$ to $10^{2} \mu m$.

The presence of NaCl and KCl can significantly reduce deposit melting point and the ease with which the deposit can be removed: Chapter 4 discusses fuming in greater detail. Recovery boilers can operate efficiently for a finite length of time, after which they must be taken off line for thorough cleaning. Cleaning is accomplished by running water through the sootblowers and washing the deposits from the heat transfer surfaces within the boiler. Mill data has shown that a water wash was required for one boiler after about 120 days: A draft loss increase across the boiler bank of 50 mm Hg was observed during the latter 30 days of operation (Tran, 1997).
After the gases pass through the superheater, they enter the steam generating bank (or boiler bank). The majority of deposit build-up takes place at the inlet of the generating bank because the flue gas temperature is high just downstream of the superheater and the tubes within the bank are tightly spaced (Tran, 1997). For chemical recovery boilers equipped with direct contact evaporators, the flue gases pass through a relatively small economizer bank.

The boiler feedwater enters the economizer at a minimum temperature of 250°F and is heated with flue gases that enter at about 800°F and exit at about 375°F (higher exit temperature if DCE is used). For corrosion prevention purposes, it is important that the flue gases stay hot enough to prevent water from condensing within the precipitator, induced draft fan, ducting, and stack. If a DCE is used, the flue gases exiting the economizer enter a cascade or cyclone type evaporator and are further cooled as they pick up vapor during concentration of heavy black liquor. Final processing of the flue gas occurs in an electrostatic precipitator where fine condensed aerosol particles are removed by ionizing them between charged plates. The particles removed are very small – most of them are at the sub-micron level – and have similar composition as the deposits found on heat transfer surfaces within the boiler. The amount of condensed material recovered in the precipitator is significant and can range from 3% to 10% of the “as fired” black liquor dry solids (Tran, 1997). The ash that is collected in the precipitator and the ash hoppers of the boiler typically re-enters the process in a mix tank where it is dispersed into black liquor just prior to firing.
Following the precipitator, the flue gas is drawn through an induced draft fan at a slight negative pressure (~ -0.3 in H\(_2\)O, gauge): The draft keeps all gases, particle flows, and flames inside the boiler. The draft also makes it possible to have open ports at the liquor guns while minimizing the risk of hot liquor and gases blowing back. Kraft recovery boiler efficiency is usually evaluated based on thermal efficiency and reduction efficiency:

\[
\eta_{\text{thermal}} = \frac{\text{heat to steam}}{\text{total heat input to boiler}}
\]

\[
\eta_{\text{reduction}} = \frac{\text{moles of sulfur converted to Na}_2\text{S}}{\text{total moles of sulfur fired through liquor guns}}
\]

Common values observed in practice for these efficiencies are \(\eta_{\text{thermal}} \sim 60\%\) and \(\eta_{\text{reduction}} \sim 95\%\), respectively.

1.2.3 Recausticizing of Kraft Pulping Chemicals

The completion of the kraft chemical recovery cycle occurs when the sodium carbonate in green liquor is converted to caustic soda. Figure 1.20 shows a process diagram of a kraft caustic plant. In a kraft mill, the smelt that pours from the chemical recovery boiler is mixed with “weak wash” at the smelt dissolver. The solution is then pumped to large green liquor clarifiers (see Figure 1.21-1) where impurities settle out. The impurities, termed “dregs,” are concentrated and washed to recover sodium carbonate and sodium sulfide prior to disposal. Dregs contain mostly iron and calcium, as well as some unburned carbon. The clarified
Figure 1.20 Kraft Process Caustic Plant
green liquor is pumped to the slaker (see Figure 1.21-2) where quicklime (CaO) is added to the solution under heavy agitation. The quicklime added to the slaker reacts exothermically with water to form slaked lime (Ca(OH)_2).

\textit{Equation 1.24: Slaking} \quad \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{energy}

Unreacted particles (grits) settle out in the slaker and are washed prior to disposal. The causticizing reaction begins in the slaker and continues as the liquor passes through a series of continuously stirred reactors called causticizers. White liquor is discharged from the causticizers and clarified in the same way that green liquor is clarified (see Figure 1.21-3).

The clarified white liquor is ready for use as kraft pulping liquor and is pumped to the pulp mill. The conversion of sodium carbonate to sodium hydroxide is evaluated through titration of the white liquor to determine the causticizing efficiency. The causticizing efficiency is commonly observed to be \(~90\%\) in many caustic plants.

\textit{Equation 1.26} \quad \eta_{\text{causticizing}} = 100\% \times \left( \frac{\text{NaOH}}{\text{NaOH} + \text{Na}_2\text{CO}_3} \right)

Other white liquor properties are determined as discussed in §1.1.2.2.2 equations 1.13 through 1.16. The total titratable alkali (equation 1.13) of clarified white liquor usually ranges between 6 lb/ft\(^3\) and 8 lb/ft\(^3\). The precipitate that settles out in the white liquor clarifier is lime mud (CaCO\(_3\)). Lime mud is washed and filtered (see Figure 1.21-4) prior to re-burning in lime kilns (Figure 1.21-5).
Figure 1.21 Kraft Caustic Plant Equipment: (1) green liquor clarifiers and lime kilns; (2) lime silos, slaker, causticizers, and grit system; (3) white liquor clarifier; (4) lime mud filter; (5) pebbles of calcined lime exiting a lime kiln at 1800°F.
The calcining process, or conversion of lime mud to quicklime, is ancient and is also used for the manufacture of concrete. The calcining process is endothermic and requires sufficient temperature (~1800°F) and time to convert lime mud to quick lime. Lime mud enters the kiln at about 68% solids and is initially dried and heated. The kiln slowly rotates to agitate the lime and transport it through the tubular reactor. The calcining reaction begins at about 1500°F in the last half of the reactor. Lime kilns are heated with natural gas or oil fired from the discharge end of the reactor. Due to the high temperatures involved, the lime kiln is also used to incinerate non-condensible gases produced during the pulp blowing and black liquor evaporation processes in other parts of the mill. Proper temperature control is a must during the calcining process. A cold kiln will not adequately convert lime mud to quick lime whereas a hot kiln will produce quick lime that is non-porous and relatively unreactive in the slaker. Re-burned lime is discharged from the kiln and transported to storage where additional quicklime is added as make-up. The quality of the re-burned lime is often determined using the lime availability test. The availability test determines the amount of lime available for slaking. Typical industrial values range from 87% to 91%.

Samples of pulping liquors from various stages of the Kraft and NSSC processes are shown in Figure 1.22.

In summary, the composition of black liquor can be dependent on wood species, chip quality, pulping operations, white liquor quality, and chemical
Figure 1.22 Chemical Pulping Liquors (clockwise from left): kraft black liquor, kraft green liquor (dregs at bottom of flask), kraft white liquor (lime mud bottom of flask), and NSSC sulfite liquor.
recovery operations. The combustion characteristics of kraft black liquor are largely dependent on its physical and chemical properties, as well as operation of the recovery boiler. Inadequate control of kraft chemical recovery processes leads to excessive and costly carryover of "dead load" chemicals such as saltcake, lime mud, and soda ash: For these reasons, the value of efficient operation of the recovery boiler, caustic plant, evaporators, and pulp mill cannot be over stressed.
CHAPTER 2

OBJECTIVE OF THIS STUDY

The objective of this study was to broaden the understanding of mechanisms involved with alkali metal emissions during kraft black liquor combustion. An improved understanding of the processes that lead to the vaporization of sodium during black liquor combustion was specifically sought. The fuming behavior of a single black liquor at different solids feed rates and excess oxygen levels and the variations of fuming behavior between five different black liquor solids at constant excess oxygen level was the focus of the laminar entrained flow reactor combustion study. A thorough understanding of recovery boiler fouling mechanisms is a pre-requisite for maximizing recovery boiler throughput, energy utilization, and up-time while minimizing environmental emissions.
CHAPTER 3

EXPERIMENTAL PROCEDURES

Black liquor handling procedures, experimental equipment, operational procedures, and routine reactor maintenance are presented in this chapter.

3.1 Experimental Equipment and Operations

A laminar entrained flow reactor (LEFR) was used for the combustion experiments that were performed during this study. A diagram representing the major components of the LEFR is provided in Figure 3.1. The LEFR has many important features that produce a well developed laminar flow within the reactor, promote high particle heating and cooling rates, and efficiently separate fume and char particles from one another. Referring to Figure 3.1, the reactor consists of a particle feeder, a liquid-cooled particle injector, a tubular section with three heating zones, a liquid cooled particle collector, cyclone separator, and fine particle filters.

Black liquor particles are prepared and loaded into the particle feeder. Particle feed rate is controlled primarily by the variable speed drive on the particle feeder. Primary gas is fed to the particle feeder where it entrains black liquor particles. The mixture of primary gas and black liquor particles is transported to the particle injector. The injector is constructed with an outer shell that is liquid cooled to prevent pre-mature particle heating. The particles and primary gas are
Figure 3.1 Diagram of the Laminar Entrained Flow Reactor
injected at the center of the LEFR tube. Secondary gas enters the bottom of the reactor and is passed through the outer reactor shell where it is pre-heated to the temperature of the reactor heating elements. Heated secondary gas reaches the top of the reactor and is turned 180° and passed through a flow straightening device. The primary gas and black liquor particles enter the reactor coaxially with the secondary gas in laminar flow at the top of the reactor. The black liquor particles are rapidly heated (10^4 °C/second) and react with the primary and secondary gas. The high particle heating rate is possible for a number of reasons: (1) The primary gas flow constitutes only 2.5% of the total reaction gas feed; (2) radiant heat is transferred to the gas stream from the reactor walls and burning particle cloud; and (3) sensible heat is transferred from the pre-heated secondary gas to the primary gas. The reactor is heated via three heating element zones. Each heating zone has its own temperature controller and is heated or cooled at a maximum ramp rate of 200°C/hr.

The extent to which the black liquor particles react can be controlled by adjusting the collector position inside the reactor, modifying the reaction gas flow rate, modifying the reaction gas composition, modifying the reactor temperature, or modifying the black liquor solids feed rate (as was discovered during the course of this study – see §4): All of my experimental runs were performed with identical collector position, reaction gas flows, reaction gas compositions, and reactor zone temperatures.
As the reaction gas and particles reach the exit of the reactor tube, they enter the tip of the collector where a large portion of nitrogen quench gas is passed through the porous collector tip. The collector is liquid cooled and insulated so that quench gas is not heated by the ambient environment inside zone 3 of the reactor tube. The total amount of nitrogen quench gas added from the porous collector walls is equal to the primary and secondary gas flows combined. Approximately half of the quench gas enters the reaction gas stream at the top of the porous collector, with the balance entering from the sidewalls of the collector. As the primary, secondary, and quench gases mix, reactions cease to occur and aerosols begin to condense.

The collector is designed to minimize condensation of aerosols via thermophoresis on surfaces within. The gas/particle mixture exits the collector and enters a cyclone separator tangentially where char particles are deposited in the cyclone catch reservoir. The gas stream exits the cyclone assembly and is passed through filters (0.8 μm x 9 cm diameter and 0.22 μm x 4.7 cm diameter) that collect the condensed fume particles. The duration of each combustion experiment was governed by reactor pressure. As fume deposits on the particle filters, the pressure within the LEFR rises. When a pressure of 5-6 psig was reached within the reactor, the experiment was ceased by turning off the reaction gas and the black liquor particle feeder.
3.2 Black Liquor Solids Preparation

The black liquors used in this study were donated from mills located in the United States and Finland. Table 3.1 summarizes the liquor sources and some applicable details of their processing prior to receipt at OSU. All of the liquors –

Table 3.1 Black Liquors used for this Study

<table>
<thead>
<tr>
<th>Liquor Source</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pacific Northwest United States – oxidized Douglas Fir kraft to 95 kappa number / Alder, Oak NSSC mixed black liquor</td>
</tr>
<tr>
<td>2</td>
<td>Southeastern United States – Southern Pine cooked to low kappa number for bleaching</td>
</tr>
<tr>
<td>3</td>
<td>Southeastern Atlantic Coast United States – Southern Pine cooked to low kappa number for bleaching</td>
</tr>
<tr>
<td>4</td>
<td>Finland – pre-LHT virgin black liquor Nordic Pine kraft to 24 kappa number</td>
</tr>
<tr>
<td>5</td>
<td>Southeastern United States – kraft black liquor, unknown fiber source</td>
</tr>
</tbody>
</table>

except liquor #4 - were “as fired” – meaning that they had been oxidized (if applicable), concentrated, and mixed with make-up chemicals at the donor facility. Additional details of their chemical make-up can be found in Table C.1 in Appendix C.
3.3 LEFR Set-up and Experimental Conditions

This study originally began with one main theme (I): Does sodium volatilization during kraft black liquor combustion vary from liquor to liquor? During the experimental process, a discovery was made that was not anticipated. This led to an additional theme (II): Why does sodium volatilization vary with black liquor solids feed rate in a laminar entrained flow reactor? For experiments seeking to answer the question to theme (I), all reactor conditions were held constant as listed in Table 3.2 including black liquor solids feed rate: This was

Table 3.2 LEFR Settings for Experiments Performed

<table>
<thead>
<tr>
<th>Reactor Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 1 Temperature (°C)</td>
<td>1000</td>
</tr>
<tr>
<td>Zone 2 Temperature (°C)</td>
<td>1000</td>
</tr>
<tr>
<td>Zone 3 Temperature (°C)</td>
<td>1000</td>
</tr>
<tr>
<td>Primary Gas Flow (l/min)</td>
<td>0.50</td>
</tr>
<tr>
<td>Secondary Gas Flow (l/min)</td>
<td>19.50</td>
</tr>
<tr>
<td>O₂ Flow (l/min)</td>
<td>0.80</td>
</tr>
<tr>
<td>N₂ Flow (l/min)</td>
<td>19.20</td>
</tr>
<tr>
<td>Quench Gas Flow (l/min)</td>
<td>20.00</td>
</tr>
<tr>
<td>Black Liquor Particle Size (µm)</td>
<td>63-100</td>
</tr>
<tr>
<td>BL Feed Rate (g/min)</td>
<td>0.73</td>
</tr>
<tr>
<td>Liquor-to Liquor Study- constant feed</td>
<td></td>
</tr>
<tr>
<td>BL Feed Rate (g/min)</td>
<td>0.47-1.08</td>
</tr>
<tr>
<td>Varying Solid Feed Rate Study</td>
<td></td>
</tr>
<tr>
<td>Particle Residence Time (seconds)</td>
<td>0.67</td>
</tr>
</tbody>
</table>
accomplished by setting the solids feeder control dial at the same index mark for each experiment. For experiments seeking to answer the question to theme (II), all reactor conditions were held constant as listed in Table 3.2 except black liquor solids feed rate: The feed rate was varied between 0.47 g/min and 1.63 g/min for these studies. An estimate of the black liquor particle residence time was obtained by using a modified version of Flaxman's fluid and heat transfer model of particle flow through a LEFR (Flaxman, 1987). Flaxman's model was developed for coal combustion: Modifications to the model were made to account for the swelling, devolatilization, and specific combustion characteristics of black liquor particles.

3.4 Experimental Procedure

The experimental procedure for performing black liquor combustion experiments with the laminar entrained-flow reactor includes black liquor preparation, reactor preparation, and operation; furthermore, it also includes char, fume, and black liquor solids collection, sampling, and analysis.

3.4.1 Preparation of Black Liquor Solids

Black liquor solids are prepared using a three step process which includes drying, grinding, and sieving.
3.4.1.1 Drying of Black Liquors

- Heat the black liquor by placing a sealed plastic bottle full in a warm water bath at 75°C for 1 hour. Mix the black liquor thoroughly with a stirring rod and pour a small amount into metal pans (Teflon® coated) for drying. Place the black liquors in an oven at 80-100°C.
- Once the liquor is dry and brittle (typically 24 to 48 hours), scrape it from the pans, break it into small pieces, and store it in a vacuum oven at 50°C.

3.4.1.2 Grinding and Sieving of Black Liquor Solids

- One day prior to an experimental run, remove the black liquor solids from the oven and grind them into powder with a coffee grinder. Sieve the black liquor powder with flat sieve screens to a 63-100 micron size fraction: This process must be performed quickly due to the hydrophilic nature of black liquor solids. Store the black liquor powder in a vacuum oven at 50°C in a glass container until needed for an experimental run with the LEFR. Just prior to an experimental run, cool the black liquor solids in a desiccator to avoid moisture absorption and weight measurement error. Repeat this process with all black liquors to be tested and clearly label glass storage containers.
3.4.2 Preparation of Experimental Apparatus for Combustion Experiments

Proper inspection, cleaning, assembly, and set-up are critical to the successful operation of the laminar entrained flow reactor.

3.4.2.1 Laminar Entrained Flow Reactor

- With the reactor and cooling system turned off and at room temperature, inspect the inner surfaces of the reactor, collector, and injector using a mirror and flashlight. All surfaces should be deposit free. If necessary, uncouple the injector coolant lines and remove the injector from the top of the reactor. For safety purposes, the injector should be inspected routinely for corrosion at the tip. If excessive corrosion exists, have repairs made by a reputable contractor or have a new injector fabricated: *This step is extremely important because the temperatures inside the reactor during a run are sufficient to cause a steam explosion should a leak in the injector cooling system occur.*

- Once the reactor is clean and verified to be in safe condition, adjust the collector to the desired position and pin in place. Inspect the o-ring seal at the base of the collector: Apply o-ring grease and / or replace the o-ring if necessary.
• Turn on the reactor coolant system and verify the flow through the injector, collector, and pump discharge. The coolant system must be on at all times when the LEFR is in operation.

• Set each zone temperature controller according to desired ramp time (200°C/hr maximum) and final reactor zone temperature (1000°C for the purposes of these experiments). Turn the controller off, pause for 20 seconds, and turn it back on: The controller should begin reactor zone warm up as desired. Do not leave the reactor unattended until proper ramp has been verified. Severe damage could occur to the LEFR if zone-to-zone temperature varies significantly within the reactor tube.

3.4.2.2 Black Liquor Feeder and Primary Gas Line

• Disconnect the primary gas / particle entrainment line from the particle feeder and injector. Uncouple the particle feeder head from the gas line. Clean the line and particle feeder head separately by flushing them with water and blowing them out with nitrogen gas. Place the line and particle feeder head in the laboratory oven at 100°C for at least 2 hours to ensure all moisture is absent. Re-assemble the primary gas / particle entrainment line and particle feeder head and install them on the LEFR.
3.4.2.3 Collector Cyclone, Catch Reservoir, and Filter Assembly

- Place a supply of 0.8 μm x 9 cm diameter and 0.22 μm x 4.7 cm diameter filters in the laboratory oven at 100°C.
- Disassemble collector cyclone, catch reservoir, and filter assembly by removing socket-head screws, quick disconnect clamps, and o-rings. Thoroughly wash all components of the collector assembly with soap and water and scrub out all tubing with pipe cleaning brushes. Remove all o-ring seals and inspect for damage: Apply o-ring grease and / or replace o-rings if necessary. Dry the collector components thoroughly and place them in the laboratory oven at 100°C.

3.4.3 Operation of the LEFR for Combustion Experiments

- Verify that the LEFR is at 1000°C by examining the three zone heater control outputs.
- Verify that the reactor cooling system is operating properly.
- Assemble the collector cyclone assembly using socket head screws and quick disconnect clamps. Weigh the fine particle filters and install them as necessary.
- Install the collector cyclone and the filter assembly in the bottom of the collector being careful not to damage the o-ring seal. Secure the lower collector assembly as necessary.
- Place the exhaust vent ducting near the discharge of the fine particle filters to collect gases produced during the combustion reactions. Verify that the vent fan is on and drawing air through the ducting.

- Fill a test tube with black liquor powder and weigh on the laboratory balance. Record the measurement and load the test tube into the particle feeder assembly. Make sure that a good o-ring seal is made – apply o-ring grease if necessary.

- Verify that nitrogen and oxygen pressure is adequate at the respective regulators. Turn on the quench gas to 20 l/min and the reaction feed gas to 20 l/min with O₂ at 0.80 l/min and N₂ at 19.20 l/min. Adjust the primary gas flow to 0.50 l/min.

- Turn on the black liquor feeder to the desired feed setting: 0.73 g/min feed rate (set the feeder dial at the index mark) for the liquor to liquor study and 0.47-1.08 g/min feed rate for the variable feed rate study.

- Verify that black liquor solids are being entrained by the primary reaction gas by observing fluidization of particles at the top of the test tube. If fluidized particles are not observed, shut the reactor down, document the event, and repeat all of the previous steps beginning at §3.4.2.2 making sure that the particle feeder and primary reaction gas / particle entrainment line and injector are clean and dry.

- If the experimental run is confirmed to be proceeding properly, start a timer to measure the duration of the run. Observe the reaction gas
feed and adjust as necessary. The pressure within the reactor will rise approximately linearly and reduce the gas flows slightly if they are not adjusted “on the fly.”

- The run will last for about 2 ½ minutes or until the pressure within the reactor reaches 5-6 psig, depending on the fuming characteristics of the black liquor used for the experiment.
- When the pressure in the reactor has reached 5-6 psig, close the primary gas flow and stop the particle feeder. Stop the timer and shut off all other gas flows. Record the duration of the experiment.
- Remove and disassemble the collector cyclone and filter assembly. Weigh the fine particle filters and store them in a sealed sample cup. Collect all char from the cyclone catch, weigh, and store it in a sealed sample cup. Properly label all collected samples. This procedure must be performed promptly following the experimental run due to the hydrophilic nature of the fumes and chars.
- Remove the test tube of black liquor solids from the feeder making sure all of the solids stay in the tube and weigh. Immediately store the solids in a laboratory oven at 100°C (short term) or in a vacuum oven at 50°C (long term).
- Clean all of the equipment and return to step 3.4.2.2 to perform additional experiments.
Following the completion of all experimental runs, set zone heating elements to desired storage temperature and ramp down at 200°C/hr. Turn off the controllers for 20 seconds then turn them back on. Verify that the reactor is cooling at the desired rate before leaving it unattended.

3.4.4 Black Liquor Solids, Fume, and Char Analysis

Black liquor solids, fumes from the fine particle filters, and chars from the cyclone catch were sent to the Weyerhaeuser Analytical laboratory in Tacoma, WA for analysis of total sodium, potassium, chloride, sulfate, sulfite, and thiosulfate. The results of the analysis can be found in Table C1 in Appendix C.
CHAPTER 4

RESULTS AND DISCUSSION

This chapter is divided into three sections. The results of the liquor feed rate study are presented and discussed first. Differences in fuming and sodium vaporization of the liquors involved with the liquor-to-liquor study are presented and discussed second, followed by presentation and discussion of the potassium and chloride enrichment behavior of the associated liquors that were studied.

4.1 Fuming Tendencies of Black Liquor at Varying Solids Feed Rates

Many studies have investigated the effects of temperature, residence time, and feed gas concentration during combustion and pyrolysis of black liquor particles using the laminar entrained flow reactor (Carangal, 1994; Reis et al., 1995; Phimolmas, 1996). Combustion studies have shown that fuming is a strong function of temperature and particle size. At the time that the experiments documented in this study were made (December 1996), the effects of varying solids feed rate on black liquor fuming in the laminar entrained flow reactor had not been documented. While performing experiments with liquor #3 at different solids feed rates, it was observed that fuming was greatest at low solids feed rates. The reactor set-up parameters for this study can be found in Appendix A, Tables A.2 through A.12 and data generated in Appendix B, Table B.1, and Figures B.1 and B.2.
Figure 4.1 Fume Generated as a function of BLS Feed Rate (Liquor #3)

Figure 4.2 Fume Generated as a function of Excess Oxygen (Liquor #3)
Figure 4.1 shows the fuming trend that was observed during these experiments. The amount of excess oxygen that was fed to the LEFR was estimated (see Appendix E) to provide insight into the observed differences in char appearance and fume generation. Figure 4.2 shows that the fume formation increased with increasing excess oxygen. The rate of combustion was enhanced by the excess oxygen availability at low solids feed rates. The char that was produced during these experiments varied in appearance: The char residue at low solids feed rates was nearly white and appeared to be of a consistency similar to that of a dense powder, whereas the char residue at high solids feed rates was black and porous. SEM photographs were taken of two of the chars produced during these experiments. Figures 4.3 and 4.4 show char samples from liquor #3 burned at a solids feed rate of 0.51 g/min. The particles vary in size from 15 μm to 75 μm and appear to be dense. Figures 4.5 and 4.6 show char samples from liquor #3 burned at a solids feed rate of 0.88 g/min. The char particles vary in size from 5 μm to >100 μm and appear to be very porous: These particles were black, indicating that they contained fixed carbon. These trends indicate that fume is released during the entire char burning process.

The observations may be a result of one or many combined conditions. (1) Mass transfer of oxygen may be limited within the dense particle cloud at the axis of the LEFR during high solids flow rate experiments. The temperature dependence of gas phase binary diffusion coefficients contradicts hypothesis (1): Gas phase binary diffusion coefficients have been shown to be a function of
Figure 4.3 SEM Photo of Char Particle Group Produced During Combustion of Liquor #3 at Solids Feed Rate of 0.51 g BLS/min

Figure 4.4 SEM Photo of Char Particle Cluster Produced During Combustion of Liquor #3 at Solids Feed Rate of 0.51 g BLS/min
Figure 4.5 SEM Photo of Char Particle Group Produced During Combustion of Liquor #3 at Solids Feed Rate of 0.88 g BLS/min

Figure 4.6 SEM Photo of Char Particle Cluster Produced During Combustion of Liquor #3 at Solids Feed Rate of 0.88 g BLS/min
temperature as $T^{3/2}$ for non-polar gases and as $T^{7/4}$ for polar gases (Cussler, 1984). Furthermore, since excess oxygen was always present in the reaction feed gas (primary and secondary combined, see Figure 4.2 and Appendix E), mass transfer limitations in the bulk gas seem less likely. Research performed with pulverized coal, where pulverized is defined as particles that pass through a 200 mesh screen and have a mean particle diameter of 50 µm, has shown that, for the coal-air system, three major reaction modes exist (Singer, 1984). The first mode occurs at $T < 750°C$ and is controlled by chemical kinetics. The second mode occurs in the temperature range of $600°C < T < 800°C$ and is controlled by a combination of chemical kinetics and diffusion. Particle size and porosity are important in mode two. The third mode occurs at $T > 900°C$. The reaction rate is high in mode three and takes place at the particle surface. Diffusion of oxygen to the reacting particles controls the combustion rate in mode three, especially* when particle and flow velocity are high (Kanury*, 1975). Given the similarities between coal and black liquor combustion at high temperatures, diffusion of oxygen from the bulk gas to the particles may have played an important role at high particle feed rates. The evidence of fixed carbon in chars produced during a number of these experiments indicates that, despite the abundance of oxygen in the bulk gas, complete combustion was not realized at high solids feed rates.

(2) Radiant heat transfer to liquor particles may have been hindered by particle cloud density. Char particles expand and swell a great deal as they devolatilize (see §1.2.1.3). At high black liquor solids flow rates, the expansion of
the devolatilized liquor particles may be sufficient to shield liquor particles at the axis of the reactor from radiant heat. If temperatures were lower within the particle column at the axis of the LEFR, the rate of combustion would be less, thus less heat would be generated and transferred to surrounding particles. Coal combustion research has shown that radiant heat transfer can account for 95% of the overall heat transfer particularly because of the role of high concentrations of dark colored fine fuel particles (Smoot, 1979). LEFR experiments have shown that black liquor fuming increases with oxygen concentration and temperature (Vakkilainen et al., 1995). Furthermore, a study showed that black liquor droplets burned in air can reach temperatures 300-500°C higher than their surroundings (Frederick 1994).

(3) At low solids feed rates, heat generated from combustion caused particles to swell rapidly, enhance mass transfer, and reach higher temperatures and generate more fume. It seems that, for the reactor conditions studied, one can move the combustion mechanism at the discharge of the reactor into the later char burning phase (low solids feed rate, higher excess O₂) or into the early char burning phase (high solids feed rate, lower excess O₂). *The observations made during these experiments indicate that a combination of black liquor swelling during devolatilization and related mass transfer and temperature effects, combined with bulk gas diffusion limitations may be responsible for variations in fuming behavior at different solids feed rates in a laminar entrained flow reactor.*
4.2 Differences in Black Liquor Fuming Behavior at Constant Solids Feed Rate

Black liquor fuming and sodium vaporization differences between five black liquors were investigated: The data collected during those experiments is presented and discussed in the sections that follow.

4.2.1 Liquor to Liquor Differences in Fuming

In these experiments, black liquors from five different mills were studied with the laminar entrained flow reactor (LEFR). Dry black liquor solids were fed to the LEFR with a target mass flow rate of 0.73 grams of black liquor solids/minute. Table D.1 in Appendix D summarizes the data generated during this study. For the case of liquors #1, #4, and #5, data from three successful experiments was included. For the case of liquor #2, data from four successful experiments was included. For the case of liquor #3, data from 22 successful experiments yielded regression predicted fuming information for comparison with the other liquors. Samples of black liquor, char, and fume were collected from one representative run within each group of experiments performed and were sent to the Weyerhaeuser Analytical and Testing Laboratory in Tacoma, Washington for analysis.

All data generated from experiments was included unless a known fault in the experiment was observed: Rejected experiments are highlighted in red in the tables of Appendix A. A brief description of the reason for experiment rejection
can be found in the "Notes" row of the experimental data tables. Figure 4.7 shows the average fume generated (as percentage of black liquor solids input) during the experiments performed using the five liquors previously listed. In addition, the average black liquor solids feed rate for the experiments is shown for each liquor. The fume yield for liquor #3 was calculated from the regression line generated from the solids feed rate study that is discussed in §4.1. The error bars represent calculated sample 95% confidence intervals for each set of liquor data. The graph shows that the liquor feed rate was held relatively steady for the runs. The fume data variability was least for liquors #5 and #1 and was the greatest for liquors #2 and #4. Note that the sample mean is being used as an estimate of the population mean for the purposes of calculating 95% confidence limits. Due to the time requirement of each experiment, it was not practical to run experiments greater than 30 times at each set of reactor conditions as would be required according to the Central Limit Theorem. Despite the limitations of experimental repetition, the estimated 95% confidence limit values do provide valuable measures of statistical variation.

One-way analysis of variance (ANOVA) was performed in order to provide additional statistical basis for drawing conclusions (Wadsworth, 1990). The ANOVA method tests the hypothesis that the sample means are equal by comparing the sample variances and degrees of freedom with the standard F-distribution. The tests were performed at two significance levels. The lowest significance level at which the null hypothesis was rejected was 0.035: This
Figure 4.7 Black Liquor Solids Fuming Characteristics

Figure 4.8 Sodium Content of Fumes, Chars, and Black Liquors
indicates a 0.96 certainty that liquor to liquor differences in fuming exist at nearly identical reactor conditions. The results of the ANOVA tests and additional information regarding the method are summarized in Appendix E. *Figure 4.7 and calculations summarized in Appendix E show that within the limits of the experiments performed and the capabilities of the analytical methods applied, liquor to liquor variations in fuming behavior were observed.*

Figures 4.7 through 4.12 show the distribution of sodium, chloride, potassium, sulfate, and thiosulfate, in the fumes, chars, and black liquors, respectively. There were differences in the distribution of inorganic salts in the black liquors analyzed. Figure 4.8 shows that the sodium content of liquor #2 was the lowest at 15.4% while that of liquor #3 was 20.7%. Despite these differences, the sodium concentration in the fume was nearly identical at 35.7% and 35.4%, respectively. Furthermore, Figure 4.9 shows that there was a marked difference in the anions associated with sodium in these liquors. Liquor #3 had a chloride content that was on the order of 10 times that of any of the liquors studied implying that it had a sodium chloride concentration that was 10 times that of the other liquors. The black liquors that had the highest chloride content also produced the most fume during combustion.

Figures 4.10 through 4.13 show that the potassium, sulfate, thiosulfate, and sulfite concentrations of the liquors varied to a large extent and had little impact on the overall fuming behavior of the liquors. Figures 4.11 and 4.12 show that the sulfate content of the fumes closely followed the thiosulfate content of the chars.
Figure 4.9 Chloride Content of Fumes, Chars, and Black Liquors

Figure 4.10 Potassium Content of Fumes, Chars, and Black Liquors
Figure 4.11 Sulfate Content of Fumes, Chars, and Black Liquors

Figure 4.12 Thiosulfate Content of Fumes, Chars, and Black Liquors
The liquor with the highest thiosulfate concentration in the liquor solids and char also had the highest sulfate concentration in its fume. Figure 4.13 shows that liquor #1 had a low liquor sulfite content; however, the sulfite content of the char produced during combustion was nearly two fold that of the other liquors. Transformations of sulfur species during pyrolysis of black liquor particles in a laminar entrained flow reactor have been observed (Sricharoenchaikul et al, 1997). Analysis of char samples from black liquor particles (size fraction: 90-125 μm) pyrolyzed at T≥ 1000°C and residence time of ~0.73 s have shown that Na₂S₂O₃, Na₂SO₃, and Na₂SO₄ are reduced almost completely to Na₂S. The re-oxidation of Na₂S has been observed during char sampling in air; however, this effect can be minimized by utilizing elaborate sampling techniques (Sricharoenchaikul, 1995). The maximum temperature reached during the combustion experiments at hand was likely much higher than 1000°C; therefore, sulfur species in char samples were likely dominated by Na₂S and were oxidized by excess O₂ as they cooled after they were discharged from the LEFR collector.

Charge balances were calculated (see Appendix E) for the black liquors, chars, and fumes and are reported in Figures C.4 through C.6. The balance of anions was reported as a mass percentage estimate as carbonate. Other anionic organic materials are present in black liquor (see Figure 1.7); however, this estimate provides an insight to the location of remaining cations in the black liquors, chars, and fumes. Liquors #3 and #5 produced the most fume: Both liquors had elevated chloride content and likely released more fume via
Figure 4.13 Sulfite Content of Fumes, Chars, and Black Liquors

Figure 4.14 Sodium Vaporized as a function of Black Liquor Sodium Content
vaporization of sodium chloride. Figure C.5 shows that liquor #5 had a high estimated char carbonate content; therefore, more fume may have been released via alkali carbonate or sodium phenolate reduction. The data shows that, within the accuracy of this study, fuming rate during black liquor solids combustion can vary from liquor to liquor (at constant residence time, reactor temperature, and solids feed rate). The liquors that contained the most NaCl and had the highest anionic equivalents as alkali carbonate (or other chemical species) in their chars produced the most fume. Considering the fact that the liquors used in this study were from varying geographic locations, wood species, and were produced with different pulping parameters, the organic composition of the liquors most likely was also variable.

4.2.2 Liquor to Liquor Differences in Sodium Vaporization

Sodium salts are the most concentrated compounds found in upper recovery boiler deposits. Studies have shown that vaporization of alkali carbonate during air oxidation of sodium sulfide and sodium carbonate results from sodium oxidation in the gas phase. Oxidation of sodium lowers the gas phase partial pressure and enhances vaporization of sodium from smelt (Cameron, 1987). Sodium release during black liquor pyrolysis has been studied using the laminar entrained flow reactor, single droplet furnace, and heated grid reactor (Kauppinen, 1995): These studies concluded that, "...sodium release as vapor during pyrolysis is not significant when compared to the fraction of sodium input to the boiler that is
observed downstream in the furnace.” Dayton & Frederick (1996) measured the release of sodium, potassium, sulfur, and chlorine during combustion. During those experiments, wet black liquor (37.1% solids) and dry black liquor solids (90-125 μm) were burned in 5% oxygen and 95% helium gas, respectively. The combustion products were measured using molecular beam mass spectrometry methods and indicated that wet black liquors burn in two phases while dry black liquor solids burn in four phases. Despite the differences, it was found that the greatest amount of sodium release took place during the char burning phase of the combustion process.

For the experiments at hand, sodium vaporization was calculated as the mass of sodium retained on the fine particle filter(s) divided by the mass of sodium in the input black liquor solids and was reported as a percentage. Figure 4.14 shows that the amount of sodium that was vaporized during the combustion experiments varied from 25.2% to 33.7%. In addition, Figure 4.14 shows that the sodium vaporized may be dependent on the sodium content of the liquor being burned. The trend observed is that the percentage of sodium vaporized decreases as sodium content in black liquor increases (R² = 0.58). Figure 4.8 shows that despite the variations in black liquor sodium concentration, the concentration of sodium in the fume remained relatively constant. This implies that the saturation pressure of sodium immediately surrounding the liquor particles may have been reached during the experiments. An estimate of the mole fraction of sodium in the vapor phase entering the LEFR collector was calculated (see Appendix E) and compared with
values predicted by the model developed by Wag et al (1995). The model predicted a sodium mole fraction of about 0.012 at equilibrium conditions while that estimated for the experiments was about 0.0019 using both primary and secondary air in the calculations; therefore, the combustion gases entering the collector during the experiments were not saturated with sodium. It follows that mass transfer of sodium from the burning char may be the rate limiting step for the release of sodium in the gas phase.

Liquors #2 and #5 had the lowest equivalents per gram of anions as Cl\(^-\), SO\(_4\)^{2-}, SO\(_3\)^{2-}, S\(_2\)O\(_3\)^{2-} and cations as Na\(^+\) and K\(^+\): This implies that they contained a higher organic content. Liquors #2 and #5 vaporized the most sodium at 32.0 % and 33.7 %, respectively. Of notable mention, liquor #5 had very few anions as Cl\(^-\), SO\(_4\)^{2-}, SO\(_3\)^{2-}, S\(_2\)O\(_3\)^{2-} in its char – implying a higher alkali carbonate fraction (or other) in its char. Sodium vaporization was also plotted versus black liquor potassium, chloride, sulfate, and sulfite mass fractions and no correlation appeared to be evident; however, when plotted versus black liquor thiosulfate mass fraction (see Figure 4.15), a weak correlation of decreasing sodium vaporization was observed (\(R^2 = 0.52\)). This information implies that the liquors that vaporized the least amount of sodium had a higher content of thiosulfate (probably as a salt of sodium). As discussed by Frederick (1997), oven drying of black liquor oxidizes residual sodium sulfide to sodium thiosulfate. In addition, the oxidation of black liquor is known to reduce the heating value of the fuel due to the partial oxidation of carbon compounds.
Figure 4.15 Sodium Vaporized as a function of BL Thiosulfate Content

\[ y = -2.0205x + 0.3478 \]
\[ R^2 = 0.52 \]

Figure 4.16 Black Liquor Char Residue
The liquor that volatilized the least amount of sodium (liquor #4) contained the greatest amount of potassium (2.68%) and a comparatively high amount of sodium (19.3%) and visible carbon in its swelled char. A possible explanation for the reduced sodium vaporization observed for liquor #4 may be that the liquor burned and swelled at a slower rate than the other liquors. Observations of the char residue that resulted from the experiments showed that the char was black and porous very much resembling small black kernels of popped corn. Figure 4.16 shows that the char residue yield from liquor #4 experiments was much greater than the char residue yields from the other liquors that were tested: This was likely due to black liquor organic differences resulting from the extended delignification process used to produce this liquor. Referring to Appendix E, single factor analysis of variance (ANOVA) was applied to the char data: The lowest significance level at which the null hypothesis was rejected was $1.4 \times 10^{-6}$: This would indicate a 0.999 certainty that liquor to liquor differences in char residue yield exist at nearly identical reactor conditions.

The rate of black liquor combustion is a complex process of drying, devolatilization, char burning, and smelt reactions (Frederick, 1997). The chemical make-up of black liquor governs the physical processes that take place as the liquor particles pass through the four stages of combustion. Despite the fact that they were unmeasured, organic differences between liquors are present and can be caused by variations in wood species, geography, and process requirements of individual mills (for example, pulp kappa number). *Considering the fact that the experiments*
were performed under essentially identical conditions (reactor temperature = 1000°C, target solids feed rate ~ 0.73 g/min, residence time = 0.67, etc.), the most probable explanation for the observed behavior is that black liquor solids exhibit varying rates of combustion from one liquor to another. The variation in combustion rate may be due to liquor swelling characteristics [as was observed in §4.1]. Liquors that swell fast also burn fast and produce more heat and release more sodium than liquors that swell and burn slow.

4.3 Enrichment of Potassium and Chloride in Fume Particles

Recovery boiler efficiency is dramatically affected by the heat transfer capacity of the surfaces within the boiler. As with any heat exchanger, the degree of fouling in a recovery boiler has a substantial effect on the overall capacity of the boiler to transfer heat and generate steam (Incropera, 1990; Kauppinen et al., 1995). The recovery boiler is unique because the primary fuel (black liquor) has a high capacity to generate particles that can foul the critical heat transfer surfaces within the boiler. The particles can be either coarse entrainment carry over (20 µm to 3 mm) or fine condensation fume (0.1 µm to 1 µm) (Tran, 1997). The composition of the particles deposited on the heat transfer surfaces determines the ease with which they can be removed and the tendency of them to promote further fouling. In particular, potassium and chloride significantly lower the melting point of deposits in the kraft furnace (Cameron, 1988). The lower melting point of deposits that are rich in potassium and chloride causes the deposits to become “sticky”:
These deposits continue to trap particles that are entrained in boiler gases and eventually “grow” large enough to impede gas flow in the boiler. “The processes of vaporization of NaCl and KCl in parallel with sodium and potassium carbonate reduction, which produces sodium and potassium vapor, are responsible for the volatilization of these elements (Vakkilainen, 1995).”

Useful quantities for evaluating the tendency of recovery boiler deposits to become sticky are potassium and chloride enrichment factors (Adams & Frederick, 1988; Reis et al., 1995). The potassium enrichment factor ($EF_K$) is usually defined as the molar ratio of potassium in the deposit or dust sample to that of the black liquor.

\[ EF_K = \frac{[K]/([Na]+[K])_{\text{Fume}}}{[K]/([Na]+[K])_{BL}} \]

Chloride content is typically defined as the molar ratio of chloride to the sum of sodium and potassium. The chloride enrichment factor ($EF_{Cl}$) is usually defined as the ratio of chloride content in the deposit or dust sample to that of the black liquor.

\[ EF_{Cl} = \frac{[Cl]/([Na]+[K])_{\text{Fume}}}{[Cl]/([Na]+[K])_{BL}} \]

Vakkilainen et al. (1995) reported that potassium enrichment factor data from fourteen operating recovery boilers ranged from 1 to 2.5 and that chloride enrichment factor data for the same fourteen boilers ranged from 0.3 to 6. The enrichment of potassium and chloride in the fume particles that were collected on the fine particle filter(s) following the experiments is summarized in Figure 4.17.
Table 4.1 Enrichment of Potassium and Chloride in Fume Particles

<table>
<thead>
<tr>
<th>Liquor Source</th>
<th>$\text{EF}_K$</th>
<th>$\text{EF}_{\text{Cl}}$</th>
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<tr>
<td>#1</td>
<td>1.24</td>
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<tr>
<td>#2</td>
<td>1.09</td>
<td>1.92</td>
</tr>
<tr>
<td>#3</td>
<td>1.43</td>
<td>1.58</td>
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<tr>
<td>#4</td>
<td>1.26</td>
<td>2.2</td>
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<tr>
<td>#5</td>
<td>1.16</td>
<td>1.72</td>
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<tr>
<td>Average</td>
<td>1.24</td>
<td>1.96</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.13</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Figure 4.17 Enrichment of Potassium and Chloride in Fume Particles
and Table 4.1. As was observed by Frederick et al. (1995), the chloride enrichment factors are greater than the potassium enrichment factors. When compared with the data presented by Tran (1997), the sticky temperature ($T_{STK}$) of the fumes produced during this study would lie in the range of 525°C to 700°C: This is a range that is commonly observed in operating recovery boilers.

As shown in Figure 4.9, liquor #3 had a chloride content that was approximately 10 times that of any of the other liquors. Despite the elevated level of chloride in the fume, $EF_{Cl}$ for liquor #3 was the lowest of the five liquors studied. This suggests that at high black liquor solids chloride concentrations, the level of chloride enrichment may be independent of the concentration of chloride in the black liquor solids; however, given the char observations that were made, there may be a better explanation. Char samples from liquor #3 were black and porous. They also contained elevated levels of inorganics: Liquor #3 may have burned slower, possibly due to elevated inorganic levels and swelling behavior. Studies have shown that temperature has the greatest effect on enrichment of potassium and chloride. At low temperatures potassium and chloride are readily vaporized and therefore they are enriched in upper boiler deposits at elevated levels. At high temperatures sodium release becomes increasingly dominating and condenses in the fume thereby diluting the potassium and chloride. Reis et al. (1995) found that enrichment of potassium and chloride is a strong function of temperature. The char burning model developed by Wåg et al. (1995) predicts that fume formation increases with increasing temperature and decreasing particle size and that both
potassium and chloride enrichment decrease as particle temperature increases. Frederick et al. (1998) suggests that operating recovery boilers at high temperature reduces the enrichment of potassium and chloride by diluting them with sodium sulfate and sodium carbonate. The chloride enrichment factor of liquor #3 could also have been reduced if SO₂ was present in higher concentration.
CHAPTER 5

CONCLUSIONS

The conclusions that can be drawn from the experimental results summarized in Chapter 4 are presented here.

5.1 Fuming Tendencies of Black Liquor Solids at Varying Feed Rate

The rate of black liquor combustion has a direct effect on the amount of fume (and sodium) released. Physical observations of char residues indicate that the amount of fume released is directly related to the extent of combustion. One or more of a combination of effects may be responsible for this. (1) Mass transfer of oxygen to black liquor particles may be limited in the dense particle cloud or bulk gas at high solids feed rates. (2) Radiant heat transfer to liquor particles at the axis of the reactor tube may be reduced at high solids feed rates. (3) Rapid swelling at low particle feed rates may enhance mass transfer and combustion rate allowing particles to reach higher temperatures and release more fume.
5.2 Differences in Black Liquor Fuming Behavior at Constant Solids Feed Rate

Conclusions drawn from experiments investigating black liquor fuming and sodium vaporization differences between five liquors are summarized in 5.2.1 and 5.2.2.

5.2.1 Liquor to Liquor Differences in Fuming

Fuming rate during black liquor powder combustion can vary from liquor to liquor in a laminar entrained flow reactor at the conditions used for this study. The liquors that contained the most sodium chloride and had the highest anionic equivalents as alkali carbonate (or other chemical species) released the most fume during combustion.

5.2.2 Liquor to Liquor Differences in Sodium Vaporization

Black liquor solids burn at different rates. Given nearly identical reactor conditions, black liquor char residues varied in appearance and yield indicating the presence or absence of carbon. The level of organic and inorganic material in black liquor solids appears to have an impact on the release of sodium during combustion. The liquors that contained the highest amount of sodium vaporized the least amount of sodium and vice versa. The liquors that contained the lowest inorganic cationic material released the most sodium. This may be due to
temperature differences caused by swelling variability and organic/inorganic concentration variations from liquor to liquor.

5.3 Enrichment of Potassium and Chloride in Fume

The enrichment factors measured during these experiments were slightly lower than those measured in industry. One of the liquors that was studied contained (roughly) an order of magnitude more chlorine (mass percentage); surprisingly, it had the lowest chloride enrichment factor. This indicates that the concentration of chloride in fume produced from two different black liquors burned in a laminar entrained flow reactor may be drastically different while their chloride enrichment factors remain similar.
RECOMMENDATIONS FOR FUTURE WORK

- Perform experiments at variable black liquor solids feed rates to quantify the stages of combustion most important to fuming and sodium vaporization. Perform analytical tests on samples and generate curves of (fume%, sodium volatilized, chloride volatilized) = f(solid char carbon). Thoroughly study black liquors and char samples for carbon and carbonate content and morphological properties (of chars) to assist with evaluating liquor swelling properties at different stages of the combustion process and sodium vaporization therein. Determine complete elemental analysis of all liquors, chars, and fumes.

- Perform experiments to determine the factors (organic and inorganic) that effect liquor swelling at combustion conditions and the impact on combustion and fuming rate.


APPENDICES
APPENDIX A.

EXPERIMENTAL DATA
Table A.1 LEFR Combustion Experiment Records

<table>
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<td>10/18/96</td>
<td>10/18/96</td>
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<tr>
<td>Temperature (°C)</td>
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<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Primary Flow (l/min)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Total Flow (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
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<td>0.80</td>
<td>0.80</td>
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<td>Nitrogen (l/min)</td>
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<td>19.20</td>
<td>19.20</td>
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<td>20.00</td>
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<td>new-4th pin up</td>
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</tr>
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<td><strong>Black Liquor</strong></td>
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<td></td>
</tr>
<tr>
<td>Tube + BL pre (g)</td>
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<td>18.8020</td>
<td>17.4982</td>
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<tr>
<td>Tube + BL post (g)</td>
<td>14.6563</td>
<td></td>
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</tr>
<tr>
<td>BL input mass (g)</td>
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<td></td>
<td>0.0820</td>
</tr>
<tr>
<td>BL mass flow (g/min)</td>
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<td>0.03</td>
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<td>0.0220</td>
</tr>
<tr>
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<td>Large filter pre (g)</td>
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<td>0.0189</td>
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<tr>
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<td><strong>Mass Recovery %</strong></td>
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<td></td>
<td>49.9%</td>
</tr>
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<td><strong>Notes:</strong></td>
<td>Black liquor solids: 63-100 µm powder</td>
<td>Neglect results - plugged feeder</td>
<td>Neglect results - too low of black liquor input for accuracy.</td>
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<td>Neglect results - Fume Loss - 1st run condensation</td>
<td>Feeder not working properly.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquor: #3</td>
<td>Liquor: #3</td>
<td>Liquor: #3</td>
</tr>
</tbody>
</table>

Note: Data groups that are in red print indicate that they were not included in the experimental results due to a known problem with the experiment. Details can be found in the notes row. Data groups written in italics were used for chemical analysis of liquor, char, and fume. Black liquor powder size distribution was 63 mm to 100 mm for all experiments.
# Table A.2 LEFR Combustion Experiment Records

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<tr>
<td>Temperature (°C)</td>
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<td>Total Flow (l/min)</td>
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<td>20.00</td>
<td>20.00</td>
</tr>
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<td>Oxygen (l/min)</td>
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<td>0.80</td>
<td>0.80</td>
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<td>Nitrogen (l/min)</td>
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<td>19.20</td>
<td>19.20</td>
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<td>Quench (l/min)</td>
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<td>Collector Position</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
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<tr>
<td>Run Time (min:sec)</td>
<td>2:15 to 6 psi</td>
<td>1:40 to 6 psi</td>
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<tr>
<td>Mass Balance</td>
<td></td>
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<tr>
<td>Black Liquor</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Tube + BL pre (g)</td>
<td>16.6130</td>
<td>17.1815</td>
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<tr>
<td>Tube + BL post (g)</td>
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<td>BL mass flow (g/min)</td>
<td>1.07</td>
<td>1.08</td>
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<tr>
<td>Char</td>
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<tr>
<td>Total Char (g)</td>
<td>0.7172</td>
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<tr>
<td>Char %</td>
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<td>41.3%</td>
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<tr>
<td>Fume</td>
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<td></td>
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<tr>
<td>Small filter post (g)</td>
<td>0.0952</td>
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<td>Small filter pre (g)</td>
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<td>Large filter pre (g)</td>
<td>0.2999</td>
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<tr>
<td>Total Fume (g)</td>
<td>0.3042</td>
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<tr>
<td>Fume %</td>
<td>12.7%</td>
<td>14.4%</td>
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<tr>
<td>Mass Recovery %</td>
<td>42.6%</td>
<td>55.7%</td>
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<td>#3</td>
<td>Liquor:</td>
<td>Liquor:</td>
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<td>Table A.3 LEFR Combustion Experiment Records</td>
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<td>11/17/96</td>
<td>11/17/96</td>
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<tr>
<td>Reactor Data</td>
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<tr>
<td>Temperature (°C)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Primary Flow (l/min)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Total Flow (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Oxygen (l/min)</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Nitrogen (l/min)</td>
<td>19.20</td>
<td>19.20</td>
<td>19.20</td>
</tr>
<tr>
<td>Quench (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Filter Type</td>
<td>nylon 0.8μm/0.22μm</td>
<td>nylon 0.8μm/0.22μm</td>
<td>nylon 0.8μm/0.22μm</td>
</tr>
<tr>
<td>Collector Position</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
</tr>
<tr>
<td>Run Time (min:sec)</td>
<td>2:20 to 6 psig</td>
<td>2:42 to 6 psig</td>
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</tr>
<tr>
<td>Mass Balance</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Black Liquor</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Tube + BL pre (g)</td>
<td>12.9830</td>
<td>17.7103</td>
<td>17.5215</td>
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<tr>
<td>Tube + BL post (g)</td>
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<td>BL input mass (g)</td>
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<tr>
<td>Char</td>
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<tr>
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<td>0.3176</td>
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<tr>
<td>Char %</td>
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<td>Fume</td>
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<td>Small filter post (g)</td>
<td>0.1115</td>
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<td>Small filter pre (g)</td>
<td>0.0938</td>
<td>0.0942</td>
<td>0.0920</td>
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<td>Large filter post (g)</td>
<td>0.5302</td>
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<td>Large filter pre (g)</td>
<td>0.2985</td>
<td>0.3025</td>
<td>0.3045</td>
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<td>Total Fume (g)</td>
<td>0.2494</td>
<td>0.3471</td>
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<tr>
<td>Fume %</td>
<td>12.3%</td>
<td>14.3%</td>
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<tr>
<td>Mass Recovery %</td>
<td>49.8%</td>
<td>27.5%</td>
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<tr>
<td>Notes: NOX File: FTO10014.dat</td>
<td>Smooth Run.</td>
<td>Neglect results - plugged feeder</td>
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<tr>
<td>Liquor: #3</td>
<td>Liquor: #3</td>
<td>Liquor: #3</td>
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Table A.4 LEFR Combustion Experiment Records

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<th>FTN-1701.2 rpt#2</th>
<th>FTN-1701.2 rpt#3</th>
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<td>Date</td>
<td>11/17/96</td>
<td>11/17/96</td>
<td>11/19/96</td>
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<td>Reactor Data</td>
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</tr>
<tr>
<td>Temperature (°C)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Primary Flow (l/min)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Total Flow (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Oxygen (l/min)</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Nitrogen (l/min)</td>
<td>19.20</td>
<td>19.20</td>
<td>19.20</td>
</tr>
<tr>
<td>Quench (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Filter Type</td>
<td>nylon 0.8μm</td>
<td>nylon 0.8μm</td>
<td>nylon 0.8μm</td>
</tr>
<tr>
<td>Collector Position</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
</tr>
<tr>
<td>Run Time (min:sec)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Mass Balance</td>
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<td></td>
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<tr>
<td>Tube + BL pre (g)</td>
<td>15.2356</td>
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<td>16.2737</td>
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<tr>
<td>Tube + BL post (g)</td>
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<td></td>
</tr>
<tr>
<td>BL input mass (g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BL mass flow (g/min)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Char</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Total Char (g)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Char %</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Fume</td>
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<td>Small filter post (g)</td>
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<tr>
<td>Small filter pre (g)</td>
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</tr>
<tr>
<td>Large filter post (g)</td>
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<tr>
<td>Large filter pre (g)</td>
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<td>Total Fume (g)</td>
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<td></td>
</tr>
<tr>
<td>Fume %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass Recovery %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Notes:</td>
<td>Neglect results - plugging of water contaminated collector</td>
<td>Neglect results - plugging of water contaminated collector</td>
<td>Neglect results - plugging of water contaminated collector</td>
</tr>
<tr>
<td>Liquor:</td>
<td>#3</td>
<td>#3</td>
<td>#3</td>
</tr>
</tbody>
</table>

Notes:
- Neglect results - plugging of water contaminated collector.
- Neglect results - plugging of water contaminated collector.
- Neglect results - plugging of water contaminated collector.
### Table A.5 LEFR Combustion Experiment Records

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>FTN-1701.2 rpt #4</th>
<th>FTN-1701.3</th>
<th>FTN-1701.4</th>
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<tbody>
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<td>Date</td>
<td>11/19/96</td>
<td>11/19/96</td>
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</table>

#### Reactor Data

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<tr>
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<th>FTN-1701.2 rpt #4</th>
<th>FTN-1701.3</th>
<th>FTN-1701.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Primary Flow (l/min)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Total Flow (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Oxygen (l/min)</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Nitrogen (l/min)</td>
<td>19.20</td>
<td>19.20</td>
<td>19.20</td>
</tr>
<tr>
<td>Quench (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Filter Type</td>
<td>nylon 0.8µm/0.22µm</td>
<td>nylon 0.8µm</td>
<td>nylon 0.8µm</td>
</tr>
<tr>
<td>Collector Position</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
</tr>
<tr>
<td>Run Time (min:sec)</td>
<td>3:00 to 6 psig</td>
<td>5:00 to 6 psig</td>
<td>1:50 to 6 psig</td>
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</table>

#### Mass Balance

**Black Liquor**

<table>
<thead>
<tr>
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<th>FTN-1701.3</th>
<th>FTN-1701.4</th>
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</thead>
<tbody>
<tr>
<td>Tube + BL pre (g)</td>
<td>17.9053</td>
<td>18.2131</td>
<td>17.1260</td>
</tr>
<tr>
<td>Tube + BL post (g)</td>
<td>15.8341</td>
<td>17.1273</td>
<td>15.3931</td>
</tr>
<tr>
<td>BL input mass (g)</td>
<td>2.0712</td>
<td>1.0858</td>
<td>1.7329</td>
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<tr>
<td>BL mass flow (g/min)</td>
<td>0.69</td>
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**Char**

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<th>FTN-1701.3</th>
<th>FTN-1701.4</th>
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</thead>
<tbody>
<tr>
<td>Total Char (g)</td>
<td>0.6136</td>
<td>0.4070</td>
<td>0.4873</td>
</tr>
<tr>
<td>Char %</td>
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<td>37.5%</td>
<td>28.1%</td>
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</tbody>
</table>

**Fume**

<table>
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<th>FTN-1701.3</th>
<th>FTN-1701.4</th>
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<tbody>
<tr>
<td>Small filter post (g)</td>
<td>0.5483</td>
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<td>0.5669</td>
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<td>Small filter pre (g)</td>
<td>0.3005</td>
<td>0.3039</td>
<td>0.3009</td>
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<td>Large filter post (g)</td>
<td>0.2478</td>
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<td>0.2660</td>
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<tr>
<td>Large filter pre (g)</td>
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<td>0.3039</td>
<td>0.3009</td>
</tr>
<tr>
<td>Total Fume (g)</td>
<td>12.0%</td>
<td>3.5%</td>
<td>15.3%</td>
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<tr>
<td>Fume %</td>
<td>12.0%</td>
<td>3.5%</td>
<td>15.3%</td>
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**Mass Recovery %**

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<th>FTN-1701.3</th>
<th>FTN-1701.4</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>41.6%</td>
<td>41.0%</td>
<td>43.5%</td>
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</table>

**Notes:**

- Smooth Run.
- Neglect results-suspected gas leak in system near collector.
- Smooth run.

**Liquor:**

- #3
- #3
- #3
Table A.6 LEFR Combustion Experiment Records

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<tr>
<td><strong>Reactor Data</strong></td>
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<td></td>
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</tr>
<tr>
<td>Temperature (°C)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Primary Flow (L/min)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Total Flow (L/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Oxygen (L/min)</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Nitrogen (L/min)</td>
<td>19.20</td>
<td>19.20</td>
<td>19.20</td>
</tr>
<tr>
<td>Quench (L/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Filter Type</td>
<td>nylon 0.8µm</td>
<td>nylon 0.8µm</td>
<td>nylon 0.8µm</td>
</tr>
<tr>
<td>Collector Position</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
</tr>
<tr>
<td>Run Time (min:sec)</td>
<td>2:45 to 6 psig</td>
<td>1:55 to 6 psig</td>
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</tr>
<tr>
<td><strong>Mass Balance</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>Black Liquor</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tube + BL pre (g)</td>
<td>16.7045</td>
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<tr>
<td>Tube + BL post (g)</td>
<td>15.2980</td>
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<td>BL input mass (g)</td>
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<td>BL mass flow (g/min)</td>
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<td><strong>Char</strong></td>
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</tr>
<tr>
<td>Total Char (g)</td>
<td>0.4070</td>
<td>0.3775</td>
<td>0.3128</td>
</tr>
<tr>
<td>Char %</td>
<td>26.8%</td>
<td>29.9%</td>
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</tr>
<tr>
<td><strong>Fume</strong></td>
<td></td>
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</tr>
<tr>
<td>Small filter post (g)</td>
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<tr>
<td>Large filter post (g)</td>
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<td>0.3062</td>
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<tr>
<td>Total Fume (g)</td>
<td>0.3164</td>
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</tr>
<tr>
<td>Fume %</td>
<td>22.5%</td>
<td>21.8%</td>
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</tr>
<tr>
<td><strong>Mass Recovery %</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Notes:</td>
<td>Neglect results - forgot to weigh test tube before run.</td>
<td>Smooth run. Char appears to be dense with very few pores.</td>
<td>Smooth run. Char appears to be dense with very few pores.</td>
</tr>
<tr>
<td>Liquor:</td>
<td>#3</td>
<td>#3</td>
<td>#3</td>
</tr>
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</table>


Table A.7 LEFR Combustion Experiment Records

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>FTN-2601.1</th>
<th>FTN-2601.2</th>
<th>FTD-1501.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>11/26/96</td>
<td>11/26/96</td>
<td>12/15/96</td>
</tr>
<tr>
<td><strong>Reactor Data</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Primary Flow (l/min)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Total Flow (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Oxygen (l/min)</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Nitrogen (l/min)</td>
<td>19.20</td>
<td>19.20</td>
<td>19.20</td>
</tr>
<tr>
<td>Quench (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Filter Type</td>
<td>nylon 0.8µm</td>
<td>nylon 0.8µm</td>
<td>nylon 0.8µm</td>
</tr>
<tr>
<td>Collector Position</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
</tr>
<tr>
<td>Run Time (min:sec)</td>
<td>1:43 to 5 psig</td>
<td>1:51 to 5 psig</td>
<td>1:53 to 5 psig</td>
</tr>
<tr>
<td><strong>Mass Balance</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black Liquor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tube + BL pre (g)</td>
<td>20.2634</td>
<td>18.7076</td>
<td>19.2211</td>
</tr>
<tr>
<td>Tube + BL post (g)</td>
<td>18.7076</td>
<td>17.5291</td>
<td>18.3564</td>
</tr>
<tr>
<td>BL input mass (g)</td>
<td>1.5558</td>
<td>1.1785</td>
<td>0.8647</td>
</tr>
<tr>
<td>BL mass flow (g/min)</td>
<td>0.91</td>
<td>0.64</td>
<td>0.46</td>
</tr>
<tr>
<td><strong>Char</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Char (g)</td>
<td>0.5160</td>
<td>0.3935</td>
<td>0.3199</td>
</tr>
<tr>
<td>Char %</td>
<td>33.2%</td>
<td>33.4%</td>
<td>37.0%</td>
</tr>
<tr>
<td><strong>Fume</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small filter post (g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small filter pre (g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Large filter post (g)</td>
<td>0.4954</td>
<td>0.4541</td>
<td>0.4600</td>
</tr>
<tr>
<td>Large filter pre (g)</td>
<td>0.2970</td>
<td>0.3005</td>
<td>0.2995</td>
</tr>
<tr>
<td>Total Fume (g)</td>
<td>0.1984</td>
<td>0.1536</td>
<td>0.1605</td>
</tr>
<tr>
<td>Fume %</td>
<td>12.8%</td>
<td>13.0%</td>
<td>18.6%</td>
</tr>
<tr>
<td><strong>Mass Recovery %</strong></td>
<td>45.9%</td>
<td>46.4%</td>
<td>55.6%</td>
</tr>
<tr>
<td>Notes: Smooth run.</td>
<td>Smooth run.</td>
<td>Smooth run.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reactor may be retaining fume on collector surfaces.</td>
<td>First run following reactor cleaning may have lower fume yield.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquor: #3</td>
<td>Liquor: #3</td>
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</tr>
<tr>
<td></td>
<td>Char looks dense</td>
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Table A.8 LEFR Combustion Experiment Records

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<tr>
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<th>FTD-1501.3</th>
<th>FTD-1501.4</th>
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<td>12/15/96</td>
<td>12/15/96</td>
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<tr>
<td><strong>Reactor Data</strong></td>
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<td></td>
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</tr>
<tr>
<td>Temperature (°C)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Primary Flow (l/min)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Total Flow (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Oxygen (l/min)</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Nitrogen (l/min)</td>
<td>19.20</td>
<td>19.20</td>
<td>19.20</td>
</tr>
<tr>
<td>Quench (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Filter Type</td>
<td>nylon 0.8µm</td>
<td>nylon 0.8µm/0.22µm</td>
<td>nylon 0.8µm/0.22µm</td>
</tr>
<tr>
<td>Collector Position</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
</tr>
<tr>
<td>Run Time (min:sec)</td>
<td>1:56 to 5 psig</td>
<td>1:55 to 5 psig</td>
<td>1:50 to 5 psig</td>
</tr>
<tr>
<td><strong>Mass Balance</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black Liquor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tube + BL prec (g)</td>
<td>18.3547</td>
<td>17.4510</td>
<td>16.2756</td>
</tr>
<tr>
<td>Tube + BL post (g)</td>
<td>17.4510</td>
<td>16.2756</td>
<td>15.0560</td>
</tr>
<tr>
<td>BL input mass (g)</td>
<td>0.9037</td>
<td>1.1754</td>
<td>1.2196</td>
</tr>
<tr>
<td>BL mass flow (g/min)</td>
<td>0.47</td>
<td>0.61</td>
<td>0.67</td>
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<tr>
<td>Char</td>
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<tr>
<td>Total Char (g)</td>
<td>0.2926</td>
<td>0.3668</td>
<td>0.4077</td>
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<tr>
<td>Char %</td>
<td>32.4%</td>
<td>31.2%</td>
<td>33.4%</td>
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<tr>
<td>Fume</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Small filter post (g)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Small filter prec (g)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Large filter post (g)</td>
<td>0.4900</td>
<td>0.5360</td>
<td>0.5309</td>
</tr>
<tr>
<td>Large filter prec (g)</td>
<td>0.3007</td>
<td>0.2969</td>
<td>0.2990</td>
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<tr>
<td>Total Fume (g)</td>
<td>0.1893</td>
<td>0.2391</td>
<td>0.2319</td>
</tr>
<tr>
<td>Fume %</td>
<td>20.9%</td>
<td>20.3%</td>
<td>19.0%</td>
</tr>
<tr>
<td>Mass Recovery %</td>
<td>53.3%</td>
<td>51.5%</td>
<td>52.4%</td>
</tr>
<tr>
<td><strong>Notes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smooth run. Char appears dense and is predominantly white with some small black flecks mixed in. Liquor: #3</td>
<td>Smooth run. Char appears dense and is predominantly white with some small black flecks mixed in. Liquor: #3</td>
<td>Smooth run. Char is becoming porous and black. Liquor: #3</td>
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Table A.9 LEFR Combustion Experiment Records

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>FTD-1501.5</th>
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<th>FTD-1501.7</th>
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<td>Date</td>
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<td>12/15/96</td>
<td>12/15/96</td>
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<tr>
<td><strong>Reactor Data</strong></td>
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</tr>
<tr>
<td>Temperature (°C)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Primary Flow (l/min)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Total Flow (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Oxygen (l/min)</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Quench (l/min)</td>
<td>19.20</td>
<td>19.20</td>
<td>19.20</td>
</tr>
<tr>
<td>Quench (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Filter Type</td>
<td>nylon 0.8 µm</td>
<td>nylon 0.8 µm</td>
<td>nylon 0.8 µm</td>
</tr>
<tr>
<td>Collector Position</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
</tr>
<tr>
<td>Run Time (min:sec)</td>
<td>1:49 to 5 psig</td>
<td>2:02 to 5 psig</td>
<td>1:09 to 5 psig</td>
</tr>
<tr>
<td><strong>Mass Balance</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black Liquor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tube + BL pre (g)</td>
<td>19.2750</td>
<td>15.6756</td>
<td>14.1194</td>
</tr>
<tr>
<td>Tube + BL post (g)</td>
<td>17.9702</td>
<td>14.1194</td>
<td>13.1006</td>
</tr>
<tr>
<td>BL input mass (g)</td>
<td>1.3048</td>
<td>1.5562</td>
<td>1.0188</td>
</tr>
<tr>
<td>BL mass flow (g/min)</td>
<td>0.72</td>
<td>0.77</td>
<td>0.89</td>
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<tr>
<td>Char</td>
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<tr>
<td>Total Char (g)</td>
<td>0.4334</td>
<td>0.5626</td>
<td>0.3921</td>
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<td>Char %</td>
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<td>36.2%</td>
<td>38.5%</td>
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<tr>
<td>Fume</td>
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<td></td>
</tr>
<tr>
<td>Small filter post (g)</td>
<td>0.5312</td>
<td>0.5569</td>
<td>0.4481</td>
</tr>
<tr>
<td>Small filter pre (g)</td>
<td>0.2972</td>
<td>0.3005</td>
<td>0.3000</td>
</tr>
<tr>
<td>Large filter post (g)</td>
<td>0.2319</td>
<td>0.2564</td>
<td>0.1481</td>
</tr>
<tr>
<td>Large filter pre (g)</td>
<td>0.5312</td>
<td>0.5569</td>
<td>0.4481</td>
</tr>
<tr>
<td>Total Fume (g)</td>
<td>0.2319</td>
<td>0.2564</td>
<td>0.1481</td>
</tr>
<tr>
<td>Fume %</td>
<td>17.8%</td>
<td>16.5%</td>
<td>14.5%</td>
</tr>
<tr>
<td>Mass Recovery %</td>
<td>51.0%</td>
<td>52.6%</td>
<td>53.0%</td>
</tr>
<tr>
<td><strong>Notes</strong>:</td>
<td>Smooth run.</td>
<td>Smooth run.</td>
<td>Smooth run.</td>
</tr>
<tr>
<td></td>
<td>Char is becoming porous and black.</td>
<td>Char is mostly porous and black.</td>
<td>Char is mostly porous and black.</td>
</tr>
<tr>
<td></td>
<td>Liquor: #3</td>
<td>Liquor: #3</td>
<td>Liquor: #3</td>
</tr>
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Table A.10 LEFR Combustion Experiment Records

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<th>Experiment #</th>
<th>FTD-1701.1</th>
<th>FTD-1701.1 rpt.#1</th>
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<td>Date</td>
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<td>12/17/96</td>
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<tr>
<td>Reactor Data</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Primary Flow (l/min)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Total Flow (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Oxygen (l/min)</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Nitrogen (l/min)</td>
<td>19.20</td>
<td>19.20</td>
<td>19.20</td>
</tr>
<tr>
<td>Quench (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Filter Type</td>
<td>nylon 0.8μm/0.22μm</td>
<td>nylon 0.8μm/0.22μm</td>
<td>nylon 0.8μm/0.22μm</td>
</tr>
<tr>
<td>Collector Position</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
</tr>
<tr>
<td>Run Time (min:sec)</td>
<td>2:44 to 5 psig</td>
<td>1:52 to 5 psig</td>
<td>1:50 to 5 psig</td>
</tr>
<tr>
<td>Mass Balance</td>
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<td></td>
</tr>
<tr>
<td>Black Liquor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tube + BL pre (g)</td>
<td>18.7927</td>
<td>19.2940</td>
<td>17.6566</td>
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<tr>
<td>Tube + BL post (g)</td>
<td>17.8714</td>
<td>17.6566</td>
<td>16.1830</td>
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<td>BL input mass (g)</td>
<td>0.9213</td>
<td>1.6374</td>
<td>1.4736</td>
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<td>BL mass flow (g/min)</td>
<td>0.34</td>
<td>0.88</td>
<td>0.80</td>
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<tr>
<td>Char</td>
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<td></td>
</tr>
<tr>
<td>Total Char (g)</td>
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<tr>
<td>Char %</td>
<td>34.0%</td>
<td>36.3%</td>
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</tr>
<tr>
<td>Fume</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small filter post (g)</td>
<td>0.0901</td>
<td>0.0990</td>
<td>0.1002</td>
</tr>
<tr>
<td>Small filter pre (g)</td>
<td>0.0894</td>
<td>0.0905</td>
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<tr>
<td>Large filter post (g)</td>
<td>0.2987</td>
<td>0.5360</td>
<td>0.5172</td>
</tr>
<tr>
<td>Large filter pre (g)</td>
<td>0.2980</td>
<td>0.2929</td>
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</tr>
<tr>
<td>Total Fume (g)</td>
<td>0.2476</td>
<td>0.2340</td>
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</tr>
<tr>
<td>Fume %</td>
<td>15.1%</td>
<td>15.9%</td>
<td></td>
</tr>
<tr>
<td>Mass Recovery %</td>
<td>49.2%</td>
<td>52.2%</td>
<td></td>
</tr>
<tr>
<td>Notes:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neglect results - reactor plugged mid-run.</td>
<td>NOX File: FTD17011.dat</td>
<td>NOX File: FTD17012.dat</td>
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</tr>
<tr>
<td>Liquor:</td>
<td>#3</td>
<td></td>
<td>#3</td>
</tr>
<tr>
<td>Smooth run.</td>
<td></td>
<td></td>
<td>Smooth run.</td>
</tr>
<tr>
<td>Char is porous/black</td>
<td></td>
<td></td>
<td>Char is fairly dense with a small amount of carbon.</td>
</tr>
<tr>
<td>Liquor:</td>
<td>#3</td>
<td></td>
<td>#3</td>
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</tbody>
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# Table A.11 LEFR Combustion Experiment Records

<table>
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<th>FTD-1701.3</th>
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<th>FTD-1701.5</th>
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## Reactor Data

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</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Primary Flow (l/min)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Total Flow (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Oxygen (l/min)</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Nitrogen (l/min)</td>
<td>19.20</td>
<td>19.20</td>
<td>19.20</td>
</tr>
<tr>
<td>Quench (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Filter Type</td>
<td>nylon 0.8μm</td>
<td>nylon 0.8μm/0.22μm</td>
<td>nylon 0.8μm/0.22μm</td>
</tr>
<tr>
<td>Collector Position</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
</tr>
<tr>
<td>Run Time (min:sec)</td>
<td>1:50 to 5 psig</td>
<td>2:00 to 5 psig</td>
<td>1:49 to 5 psig</td>
</tr>
</tbody>
</table>

## Mass Balance

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Black Liquor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tube + BL pre (g)</td>
<td>16.1830</td>
<td>18.7520</td>
<td>17.5079</td>
</tr>
<tr>
<td>Tube + BL post (g)</td>
<td>14.7206</td>
<td>17.5079</td>
<td>16.5409</td>
</tr>
<tr>
<td>BL input mass (g)</td>
<td>1.4624</td>
<td>1.2441</td>
<td>0.9670</td>
</tr>
<tr>
<td>BL mass flow (g/min)</td>
<td>0.80</td>
<td>0.62</td>
<td>0.53</td>
</tr>
<tr>
<td>Char</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Char (g)</td>
<td>0.4641</td>
<td>0.3837</td>
<td>0.2686</td>
</tr>
<tr>
<td>Char %</td>
<td>31.7%</td>
<td>30.8%</td>
<td>27.8%</td>
</tr>
<tr>
<td>Fume</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small filter post (g)</td>
<td>0.1035</td>
<td>0.1001</td>
<td>0.0969</td>
</tr>
<tr>
<td>Small filter pre (g)</td>
<td>0.0937</td>
<td>0.0922</td>
<td>0.0903</td>
</tr>
<tr>
<td>Large filter post (g)</td>
<td>0.5373</td>
<td>0.4943</td>
<td>0.4799</td>
</tr>
<tr>
<td>Large filter pre (g)</td>
<td>0.2986</td>
<td>0.3012</td>
<td>0.2976</td>
</tr>
<tr>
<td>Total Fume (g)</td>
<td>0.2485</td>
<td>0.2010</td>
<td>0.1889</td>
</tr>
<tr>
<td>Fume %</td>
<td>17.0%</td>
<td>16.2%</td>
<td>19.5%</td>
</tr>
<tr>
<td>Mass Recovery %</td>
<td>48.7%</td>
<td>47.0%</td>
<td>47.3%</td>
</tr>
</tbody>
</table>

## Notes

- Smooth run. Char is fairly dense and contains small amount of carbon.
- Liquor: #3
- NOX File: FTD17014.dat
- Char is fairly dense and contains small amount of carbon.
- Liquor: #3
- NOX File: FTD17015.dat
- Char is fairly dense and appears absent of carbon.
- Liquor: #3
## Table A.12 LEFR Combustion Experiment Records

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>FTD-1701.6</th>
<th>FTD-1901.1</th>
<th>FTD-1901.2</th>
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</thead>
<tbody>
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<td>Date</td>
<td>12/17/96</td>
<td>12/19/96</td>
<td>12/19/96</td>
</tr>
<tr>
<td><strong>Reactor Data</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Primary Flow (l/min)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Total Flow (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Oxygen (l/min)</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Nitrogen (l/min)</td>
<td>19.20</td>
<td>19.20</td>
<td>19.20</td>
</tr>
<tr>
<td>Quench (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Filter Type</td>
<td>nylon 0.8μm/0.22μm</td>
<td>nylon 0.8 μm/0.22 μm</td>
<td>nylon 0.8μm/0.22μm</td>
</tr>
<tr>
<td>Collector Position</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
</tr>
<tr>
<td>Run Time (min:sec)</td>
<td>2:40 to 5 psig</td>
<td>2:17 to 5 psig</td>
<td>2:22 to 5 psig</td>
</tr>
<tr>
<td><strong>Mass Balance</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black Liquor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tube + BL pre (g)</td>
<td>16.5409</td>
<td>20.4057</td>
<td>18.6760</td>
</tr>
<tr>
<td>Tube + BL post (g)</td>
<td>15.2940</td>
<td>18.6760</td>
<td>16.9249</td>
</tr>
<tr>
<td>BL input mass (g)</td>
<td>1.2469</td>
<td>1.7297</td>
<td>1.7511</td>
</tr>
<tr>
<td>BL mass flow (g/min)</td>
<td>0.47</td>
<td>0.76</td>
<td>0.74</td>
</tr>
<tr>
<td><strong>Char</strong></td>
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</tr>
<tr>
<td>Total Char (g)</td>
<td>0.4513</td>
<td>0.4259</td>
<td>0.5013</td>
</tr>
<tr>
<td>Char %</td>
<td>36.2%</td>
<td>24.6%</td>
<td>28.6%</td>
</tr>
<tr>
<td><strong>Fume</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small filter post (g)</td>
<td>0.1014</td>
<td>0.0970</td>
<td>0.1027</td>
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<tr>
<td>Small filter pre (g)</td>
<td>0.0910</td>
<td>0.0897</td>
<td>0.0927</td>
</tr>
<tr>
<td>Large filter post (g)</td>
<td>0.5260</td>
<td>0.5422</td>
<td>0.5545</td>
</tr>
<tr>
<td>Large filter pre (g)</td>
<td>0.3023</td>
<td>0.2966</td>
<td>0.2971</td>
</tr>
<tr>
<td>Total Fume (g)</td>
<td>0.2341</td>
<td>0.2529</td>
<td>0.2674</td>
</tr>
<tr>
<td>Fume %</td>
<td>18.8%</td>
<td>14.6%</td>
<td>15.3%</td>
</tr>
<tr>
<td><strong>Mass Recovery %</strong></td>
<td>55.0%</td>
<td>39.2%</td>
<td>43.9%</td>
</tr>
</tbody>
</table>

### Notes:
- NOX File: FTD17016.dat
  - Char is fairly dense and appears absent of carbon.
- Liquor: #3

- NOX File: FTD19011.dat
  - Char is fairly dense and appears absent of carbon.
- Liquor: #1

- NOX File: FTD19012.dat
  - Char is fairly dense and appears absent of carbon.
- Liquor: #1
## Table A.13 LEFR Combustion Experiment Records

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>FTD-1901.3</th>
<th>FTD-1902.1</th>
<th>FTD-1902.2</th>
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<tbody>
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<td>12/19/96</td>
<td>12/19/96</td>
<td>12/19/96</td>
</tr>
<tr>
<td>Reactor Data</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Primary Flow (l/min)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Total Flow (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Oxygen (l/min)</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Nitrogen (l/min)</td>
<td>19.20</td>
<td>19.20</td>
<td>19.20</td>
</tr>
<tr>
<td>Quench (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Filter Type</td>
<td>nylon 0.8μm/0.22μm</td>
<td>nylon 0.8 μm/0.22 μm</td>
<td>nylon 0.8μm/0.22μm</td>
</tr>
<tr>
<td>Collector Position</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
</tr>
<tr>
<td>Run Time (min:sec)</td>
<td>2:26 to 5 psig</td>
<td>2:32 to 5 psig</td>
<td>1:15 &lt; 5 psig</td>
</tr>
<tr>
<td>Mass Balance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black Liquor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tube + BL pre (g)</td>
<td>16.9249</td>
<td>20.2260</td>
<td>18.3743</td>
</tr>
<tr>
<td>Tube + BL post (g)</td>
<td>15.0946</td>
<td>18.3743</td>
<td>17.4763</td>
</tr>
<tr>
<td>BL input mass (g)</td>
<td>1.8303</td>
<td>1.8517</td>
<td>0.8980</td>
</tr>
<tr>
<td>BL mass flow (g/min)</td>
<td>0.75</td>
<td>0.73</td>
<td>0.72</td>
</tr>
<tr>
<td>Char</td>
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<td></td>
<td></td>
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<tr>
<td>Total Char (g)</td>
<td>0.5636</td>
<td>0.8304</td>
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<tr>
<td>Char %</td>
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<td>44.8%</td>
<td>45.2%</td>
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<tr>
<td>Fume</td>
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<tr>
<td>Small filter post (g)</td>
<td>0.1029</td>
<td>0.1028</td>
<td>0.0965</td>
</tr>
<tr>
<td>Small filter pre (g)</td>
<td>0.0933</td>
<td>0.0923</td>
<td>0.0914</td>
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<tr>
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<td>0.5760</td>
<td>0.4423</td>
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<td>Large filter pre (g)</td>
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<td>0.2978</td>
<td>0.2990</td>
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<tr>
<td>Total Fume (g)</td>
<td>0.2593</td>
<td>0.2887</td>
<td>0.1484</td>
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<tr>
<td>Fume %</td>
<td>14.2%</td>
<td>15.6%</td>
<td>16.5%</td>
</tr>
<tr>
<td>Mass Recovery %</td>
<td></td>
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<tr>
<td>Notes: NOX File:</td>
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<td>NOX File:</td>
</tr>
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<td>FTD19013.dat</td>
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<td>FTD19021.dat</td>
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<tr>
<td>Char is fairly dense</td>
<td></td>
<td></td>
<td>Char has abundance</td>
</tr>
<tr>
<td>and appears absent</td>
<td></td>
<td></td>
<td>of carbon.</td>
</tr>
<tr>
<td>of carbon.</td>
<td>Liquor: #1</td>
<td></td>
<td>Liquor: #4</td>
</tr>
</tbody>
</table>

Char has abundance of carbon. Run cut short due to spinning feeder. Liquor: #4
Table A.14 LEFR Combustion Experiment Records

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>FTD-1902.3</th>
<th>FTD-1902.4</th>
<th>FTD-1902.4 rpt#1</th>
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<td>Date</td>
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<td>12/19/96</td>
<td>12/19/96</td>
</tr>
<tr>
<td>Reactor Data</td>
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</tr>
<tr>
<td>Temperature (°C)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Primary Flow (l/min)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Total Flow (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Oxygen (l/min)</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Nitrogen (l/min)</td>
<td>19.20</td>
<td>19.20</td>
<td>19.20</td>
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<tr>
<td>Quench (l/min)</td>
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<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Filter Type</td>
<td>nylon 0.8μm/0.22μm</td>
<td>nylon 0.8μm/0.22μm</td>
<td>nylon 0.8μm/0.22μm</td>
</tr>
<tr>
<td>Collector Position</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
</tr>
<tr>
<td>Run Time (min:sec)</td>
<td>0:42 &lt; 5 psig</td>
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<tr>
<td>Mass Balance</td>
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</tr>
<tr>
<td>Black Liquor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tube + BL pre (g)</td>
<td>17.4763</td>
<td>19.0085</td>
<td>18.3833</td>
</tr>
<tr>
<td>Tube + BL post (g)</td>
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<td>BL input mass (g)</td>
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</tr>
<tr>
<td>BL mass flow (g/min)</td>
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<tr>
<td>Char</td>
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<td>Total Char (g)</td>
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</tr>
<tr>
<td>Fume</td>
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</tr>
<tr>
<td>Small filter post (g)</td>
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</tr>
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<td>Small filter pre (g)</td>
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<td>0.0898</td>
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<tr>
<td>Large filter post (g)</td>
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<tr>
<td>Large filter pre (g)</td>
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<td>0.3035</td>
<td>0.3004</td>
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<tr>
<td>Total Fume (g)</td>
<td>0.0727</td>
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</tr>
<tr>
<td>Fume %</td>
<td>14.0%</td>
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<td>Mass Recovery %</td>
<td>58.4%</td>
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<td>Neglect results-</td>
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<td></td>
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<tr>
<td>spinning feeder</td>
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</tr>
<tr>
<td>Char has abundance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>of carbon.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run cut short due to</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>spinning feeder.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquor:</td>
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<td></td>
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</tr>
<tr>
<td>#4</td>
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Table A.15 LEFR Combustion Experiment Records

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<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Primary Flow (l/min)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Total Flow (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Oxygen (l/min)</td>
<td>19.20</td>
<td>19.20</td>
<td>19.20</td>
</tr>
<tr>
<td>Quench (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Filter Type</td>
<td>nylon 0.8μm/0.22μm</td>
<td>nylon 0.8μm/0.22μm</td>
<td>nylon 0.8μm/0.22μm</td>
</tr>
<tr>
<td>Collector Position</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
</tr>
<tr>
<td>Run Time (min:sec)</td>
<td>2:04 to 5 psig</td>
<td>2:20 to 5 psig</td>
<td></td>
</tr>
<tr>
<td>Mass Balance Black Liquor</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Tube + BL pre (g)</td>
<td>18.0996</td>
<td>18.6320</td>
<td>20.6400</td>
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<tr>
<td>Tube + BL post (g)</td>
<td>17.4450</td>
<td>17.1233</td>
<td>18.9490</td>
</tr>
<tr>
<td>BL input mass (g)</td>
<td>0.6546</td>
<td>1.5087</td>
<td>1.6910</td>
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<td>BL mass flow (g/min)</td>
<td>0.73</td>
<td>0.72</td>
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</tr>
<tr>
<td>Char</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Char (g)</td>
<td>0.3200</td>
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<td>0.5042</td>
</tr>
<tr>
<td>Char %</td>
<td>48.9%</td>
<td>31.5%</td>
<td>29.8%</td>
</tr>
<tr>
<td>Fume</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small filter post (g)</td>
<td>0.0936</td>
<td>0.1053</td>
<td>0.1002</td>
</tr>
<tr>
<td>Small filter pre (g)</td>
<td>0.0899</td>
<td>0.0892</td>
<td>0.0900</td>
</tr>
<tr>
<td>Large filter post (g)</td>
<td>0.4129</td>
<td>0.5245</td>
<td>0.5680</td>
</tr>
<tr>
<td>Large filter pre (g)</td>
<td>0.2960</td>
<td>0.2974</td>
<td>0.2965</td>
</tr>
<tr>
<td>Total Fume (g)</td>
<td>0.1206</td>
<td>0.2432</td>
<td>0.2817</td>
</tr>
<tr>
<td>Fume %</td>
<td>18.4%</td>
<td>16.1%</td>
<td>16.7%</td>
</tr>
<tr>
<td>Mass Recovery %</td>
<td>67.3%</td>
<td>47.6%</td>
<td>46.5%</td>
</tr>
</tbody>
</table>

Notes: Neglect results-spinning feeder NOX File: FTD22011.dat Smooth run. Char has abundance of carbon. NOX File: FTD22012.dat Smooth run. Char has abundance of carbon, a bit less than FTD-2201.1 Liquor: #4 Liquor: #5
Table A.16 LEFR Combustion Experiment Records

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>FTD-2201.3</th>
<th>FTD-2202.1</th>
<th>FTD-2202.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>12/22/96</td>
<td>12/22/96</td>
<td>12/22/96</td>
</tr>
<tr>
<td><strong>Reactor Data</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Primary Flow (l/min)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Total Flow (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Oxygen (l/min)</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Nitrogen (l/min)</td>
<td>19.20</td>
<td>19.20</td>
<td>19.20</td>
</tr>
<tr>
<td>Quench (l/min)</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>Filter Type</td>
<td>nylon 0.8µm/0.22µm</td>
<td>nylon 0.8 µm/0.22 µm</td>
<td>nylon 0.8µm/0.22µm</td>
</tr>
<tr>
<td>Collector Position</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
</tr>
<tr>
<td>Run Time (min:sec)</td>
<td>2:28 to 5 psig</td>
<td>2:20 to 5 psig</td>
<td>2:28 to 5 psig</td>
</tr>
<tr>
<td><strong>Mass Balance</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black Liquor Tube + BL pre (g)</td>
<td>18.9490</td>
<td>19.5527</td>
<td>17.9275</td>
</tr>
<tr>
<td>Tube + BL post (g)</td>
<td>17.1823</td>
<td>17.9275</td>
<td>16.0510</td>
</tr>
<tr>
<td>BL input mass (g)</td>
<td>1.7667</td>
<td>1.6252</td>
<td>1.8765</td>
</tr>
<tr>
<td>BL mass flow (g/min)</td>
<td>0.72</td>
<td>0.70</td>
<td>0.76</td>
</tr>
<tr>
<td>Char Total Char (g)</td>
<td>0.5477</td>
<td>0.5348</td>
<td>0.6146</td>
</tr>
<tr>
<td>Char %</td>
<td>31.0%</td>
<td>32.9%</td>
<td>32.8%</td>
</tr>
<tr>
<td>Fume Small filter post (g)</td>
<td>0.1044</td>
<td>0.0793</td>
<td>0.1045</td>
</tr>
<tr>
<td>Small filter pre (g)</td>
<td>0.0923</td>
<td>0.0678</td>
<td>0.0927</td>
</tr>
<tr>
<td>Large filter post (g)</td>
<td>0.5920</td>
<td>0.5102</td>
<td>0.5674</td>
</tr>
<tr>
<td>Large filter pre (g)</td>
<td>0.3005</td>
<td>0.2976</td>
<td>0.2992</td>
</tr>
<tr>
<td>Total Fume (g)</td>
<td>0.3036</td>
<td>0.2241</td>
<td>0.2800</td>
</tr>
<tr>
<td>Fume %</td>
<td>17.2%</td>
<td>13.8%</td>
<td>14.9%</td>
</tr>
<tr>
<td>Mass Recovery %</td>
<td>48.2%</td>
<td>46.7%</td>
<td>47.7%</td>
</tr>
<tr>
<td><strong>Notes</strong></td>
<td></td>
<td></td>
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<tr>
<td>NOX File: FTD22013.dat</td>
<td>Smooth run.</td>
<td>Char has abundance of carbon, similar to FTD-2201.2</td>
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</tr>
<tr>
<td>Liquor: #5</td>
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<td></td>
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</tr>
<tr>
<td>NOX File: FTD22021.dat</td>
<td>Smooth run.</td>
<td>Char has abundance of carbon.</td>
<td></td>
</tr>
<tr>
<td>Liquor: (softwood) #2</td>
<td></td>
<td></td>
<td>Liquor: (softwood) #2</td>
</tr>
<tr>
<td>Table A.17 LEFR Combustion Experiment Records</td>
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<td></td>
</tr>
<tr>
<td>---------------------------------------------</td>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>Experiment #</strong></td>
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<td>FTD-2202.4</td>
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</tr>
<tr>
<td><strong>Date</strong></td>
<td>12/22/96</td>
<td>12/22/96</td>
<td></td>
</tr>
<tr>
<td><strong>Reactor Data</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>Temperature (°C)</strong></td>
<td>1000</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td><strong>Primary Flow (l/min)</strong></td>
<td>0.50</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td><strong>Total Flow (l/min)</strong></td>
<td>20.00</td>
<td>20.00</td>
<td></td>
</tr>
<tr>
<td><strong>Oxygen (l/min)</strong></td>
<td>0.80</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td><strong>Nitrogen (l/min)</strong></td>
<td>19.20</td>
<td>19.20</td>
<td></td>
</tr>
<tr>
<td><strong>Quench (l/min)</strong></td>
<td>20.00</td>
<td>20.00</td>
<td></td>
</tr>
<tr>
<td><strong>Filter Type</strong></td>
<td>nylon 0.8μm/0.22μm</td>
<td>nylon 0.8μm/0.22μm</td>
<td></td>
</tr>
<tr>
<td><strong>Collector Position</strong></td>
<td>new-4th pin up</td>
<td>new-4th pin up</td>
<td></td>
</tr>
<tr>
<td><strong>Run Time (min:sec)</strong></td>
<td>2:25</td>
<td>2:30</td>
<td></td>
</tr>
<tr>
<td><strong>Mass Balance</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Black Liquor</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tube + BL pre (g)</td>
<td>16.0510</td>
<td>17.8779</td>
<td></td>
</tr>
<tr>
<td>Tube + BL post (g)</td>
<td>14.2669</td>
<td>16.0662</td>
<td></td>
</tr>
<tr>
<td>BL input mass (g)</td>
<td>1.7841</td>
<td>1.8117</td>
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</tr>
<tr>
<td>BL mass flow (g/min)</td>
<td>0.74</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td><strong>Char</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Char (g)</td>
<td>0.5383</td>
<td>0.6354</td>
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</tr>
<tr>
<td>Char %</td>
<td>30.2%</td>
<td>35.1%</td>
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</tr>
<tr>
<td><strong>Fume</strong></td>
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<td></td>
</tr>
<tr>
<td>Small filter post (g)</td>
<td>0.1089</td>
<td>0.1133</td>
<td></td>
</tr>
<tr>
<td>Small filter pre (g)</td>
<td>0.0930</td>
<td>0.0958</td>
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</tr>
<tr>
<td>Large filter post (g)</td>
<td>0.5760</td>
<td>0.5258</td>
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</tr>
<tr>
<td>Large filter pre (g)</td>
<td>0.2978</td>
<td>0.2999</td>
<td></td>
</tr>
<tr>
<td>**Total Fume (g)</td>
<td>0.2941</td>
<td>0.2434</td>
<td></td>
</tr>
<tr>
<td>Fume %</td>
<td>16.5%</td>
<td>13.4%</td>
<td></td>
</tr>
<tr>
<td><strong>Mass Recovery %</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Notes</strong></td>
<td>NOX File:</td>
<td>NOX File:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FTD22023.dat</td>
<td>FTD22024.dat</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Smooth run.</td>
<td>Smooth run.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Char has abundance of carbon.</td>
<td>Char has abundance of carbon.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(fume #’s look high)</td>
<td>Liquor: (softwood) #2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquor: (softwood) #2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX B.

LIQUOR SOLIDS FEED RATE STUDY DATA
Table B.1 Reproducibility Study: Liquor #3

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>Solids Feed Rate (g BL/min)</th>
<th>Fume Generated (% of BL input)</th>
<th>Oxygen Requirement (mol O2/g BL)</th>
<th>Oxygen Requirement (mol O2/min)</th>
<th>O2 Feed Rate (stand. L/min)</th>
<th>O2 Feed Rate (mol/min)</th>
<th>Excess O2 (%)</th>
<th>Char Residue (% of BL input)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rpt#3 FTO-1001.2</td>
<td>1.07</td>
<td>12.7</td>
<td>0.027</td>
<td>0.029</td>
<td>0.80</td>
<td>0.036</td>
<td>25%</td>
<td>29.9%</td>
</tr>
<tr>
<td>FTO-1001.3</td>
<td>1.08</td>
<td>14.4</td>
<td>0.027</td>
<td>0.029</td>
<td>0.80</td>
<td>0.036</td>
<td>24%</td>
<td>41.3%</td>
</tr>
<tr>
<td>FTO-1001.4</td>
<td>0.87</td>
<td>12.3</td>
<td>0.027</td>
<td>0.023</td>
<td>0.80</td>
<td>0.036</td>
<td>54%</td>
<td>37.6%</td>
</tr>
<tr>
<td>FTN-1701.1</td>
<td>0.90</td>
<td>14.3</td>
<td>0.027</td>
<td>0.024</td>
<td>0.80</td>
<td>0.036</td>
<td>49%</td>
<td>13.1%</td>
</tr>
<tr>
<td>rpt#4 FTN-1701.2</td>
<td>0.69</td>
<td>12.0</td>
<td>0.027</td>
<td>0.018</td>
<td>0.80</td>
<td>0.036</td>
<td>94%</td>
<td>29.6%</td>
</tr>
<tr>
<td>FTN-1701.4</td>
<td>0.95</td>
<td>15.3</td>
<td>0.027</td>
<td>0.025</td>
<td>0.80</td>
<td>0.036</td>
<td>41%</td>
<td>28.1%</td>
</tr>
<tr>
<td>rpt#1 FTN-1701.5</td>
<td>0.51</td>
<td>22.5</td>
<td>0.027</td>
<td>0.014</td>
<td>0.80</td>
<td>0.036</td>
<td>162%</td>
<td>26.8%</td>
</tr>
<tr>
<td>FTN-1701.6</td>
<td>0.55</td>
<td>21.8</td>
<td>0.027</td>
<td>0.015</td>
<td>0.80</td>
<td>0.036</td>
<td>143%</td>
<td>29.9%</td>
</tr>
<tr>
<td>FTN-2601.1</td>
<td>0.91</td>
<td>12.8</td>
<td>0.027</td>
<td>0.024</td>
<td>0.80</td>
<td>0.036</td>
<td>47%</td>
<td>33.2%</td>
</tr>
<tr>
<td>FTD-1501.1</td>
<td>0.46</td>
<td>18.6</td>
<td>0.027</td>
<td>0.012</td>
<td>0.80</td>
<td>0.036</td>
<td>191%</td>
<td>37.0%</td>
</tr>
<tr>
<td>FTD-1501.2</td>
<td>0.47</td>
<td>20.9</td>
<td>0.027</td>
<td>0.013</td>
<td>0.80</td>
<td>0.036</td>
<td>185%</td>
<td>32.4%</td>
</tr>
<tr>
<td>FTD-1501.3</td>
<td>0.61</td>
<td>20.3</td>
<td>0.027</td>
<td>0.016</td>
<td>0.80</td>
<td>0.036</td>
<td>119%</td>
<td>31.2%</td>
</tr>
<tr>
<td>FTD-1501.4</td>
<td>0.67</td>
<td>19.0</td>
<td>0.027</td>
<td>0.018</td>
<td>0.80</td>
<td>0.036</td>
<td>100%</td>
<td>33.4%</td>
</tr>
<tr>
<td>FTD-1501.5</td>
<td>0.72</td>
<td>17.8</td>
<td>0.027</td>
<td>0.019</td>
<td>0.80</td>
<td>0.036</td>
<td>86%</td>
<td>33.2%</td>
</tr>
<tr>
<td>FTD-1501.6</td>
<td>0.77</td>
<td>16.5</td>
<td>0.027</td>
<td>0.021</td>
<td>0.80</td>
<td>0.036</td>
<td>74%</td>
<td>36.2%</td>
</tr>
<tr>
<td>FTD-1501.7</td>
<td>0.89</td>
<td>14.5</td>
<td>0.027</td>
<td>0.024</td>
<td>0.80</td>
<td>0.036</td>
<td>50%</td>
<td>38.5%</td>
</tr>
<tr>
<td>rpt#1 FTD-1701.1</td>
<td>0.88</td>
<td>15.1</td>
<td>0.027</td>
<td>0.023</td>
<td>0.80</td>
<td>0.036</td>
<td>52%</td>
<td>34.0%</td>
</tr>
<tr>
<td>FTD-1701.2</td>
<td>0.80</td>
<td>15.9</td>
<td>0.027</td>
<td>0.021</td>
<td>0.80</td>
<td>0.036</td>
<td>67%</td>
<td>36.3%</td>
</tr>
<tr>
<td>FTD-1701.3</td>
<td>0.80</td>
<td>17.0</td>
<td>0.027</td>
<td>0.021</td>
<td>0.80</td>
<td>0.036</td>
<td>67%</td>
<td>31.7%</td>
</tr>
<tr>
<td>FTD-1701.4</td>
<td>0.62</td>
<td>16.2</td>
<td>0.027</td>
<td>0.017</td>
<td>0.80</td>
<td>0.036</td>
<td>116%</td>
<td>30.8%</td>
</tr>
<tr>
<td>FTD-1701.5</td>
<td>0.53</td>
<td>19.5</td>
<td>0.027</td>
<td>0.014</td>
<td>0.80</td>
<td>0.036</td>
<td>153%</td>
<td>27.8%</td>
</tr>
<tr>
<td>FTD-1701.6</td>
<td>0.47</td>
<td>18.8</td>
<td>0.027</td>
<td>0.013</td>
<td>0.80</td>
<td>0.036</td>
<td>185%</td>
<td>36.2%</td>
</tr>
</tbody>
</table>
Figure B.1 Char Residue as a function of BLS Feed Rate (Liquor #3)

Figure B.2 Char Residue as a function of Excess Oxygen (Liquor #3)
APPENDIX C.

ANALYTICAL DATA
Table C.1 Analytical Data for Liquor to Liquor Study

<table>
<thead>
<tr>
<th>Liquor Source</th>
<th>Solids Feed Rate</th>
<th>Fume</th>
<th>Char</th>
<th>Cl</th>
<th>SO₄</th>
<th>K</th>
<th>Na</th>
<th>SO₃</th>
<th>S₂O₃</th>
<th>Cl</th>
<th>SO₄</th>
<th>K</th>
<th>Na</th>
<th>SO₃</th>
<th>S₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g/min)</td>
<td>(% BL input)</td>
<td>(% BL input)</td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
</tr>
<tr>
<td>Liquor #1</td>
<td>0.76</td>
<td>14.6</td>
<td>24.6</td>
<td>0.24</td>
<td>2.69</td>
<td>1.63</td>
<td>18.7</td>
<td>0.49</td>
<td>3.36</td>
<td>1.05</td>
<td>3.14</td>
<td>3.72</td>
<td>33.6</td>
<td>0.06</td>
<td>0.01</td>
</tr>
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<td>(FTD-1901.1)</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Liquor #2</td>
<td>0.70</td>
<td>13.8</td>
<td>32.9</td>
<td>0.29</td>
<td>1.59</td>
<td>1.37</td>
<td>15.4</td>
<td>0.96</td>
<td>2.69</td>
<td>1.3</td>
<td>17.9</td>
<td>3.48</td>
<td>35.7</td>
<td>0.3</td>
<td>0.25</td>
</tr>
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<td>(FTD-2202.1)</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Liquor #3</td>
<td>0.77</td>
<td>16.5</td>
<td>36.2</td>
<td>3.33</td>
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<td>(FTD-1902.1)</td>
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<tr>
<td>Liquor #5</td>
<td>1.16</td>
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<td></td>
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</tbody>
</table>

Average | 1.24 | 1.96 |
Standard Deviation | 0.13 | 0.33 |
Table C.2 Carbonate Estimates for Fumes, Chars, and Black Liquors

<table>
<thead>
<tr>
<th>Liquor Source</th>
<th>Fume Solids (mass %)</th>
<th>1 gram basis, equivalents</th>
<th>(mass %)</th>
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<td>SO3</td>
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<td>0.056</td>
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<td>1.3</td>
<td>17.9</td>
<td>0.25</td>
</tr>
<tr>
<td>#3</td>
<td>9.29</td>
<td>15.9</td>
<td>0.25</td>
</tr>
<tr>
<td>#4</td>
<td>0.96</td>
<td>23.4</td>
<td>0.35</td>
</tr>
<tr>
<td>#5</td>
<td>2.92</td>
<td>13.2</td>
<td>0.12</td>
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</table>

<table>
<thead>
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<th>Char Solids (mass %)</th>
<th>1 gram basis, equivalents</th>
<th>(mass %)</th>
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<td>SO3</td>
</tr>
<tr>
<td>#1</td>
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<table>
<thead>
<tr>
<th>Liquor Source</th>
<th>Black Liquor Solids (mass %)</th>
<th>1 gram basis, equivalents</th>
<th>(mass %)</th>
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<tbody>
<tr>
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<td>SO3</td>
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<td>0.89</td>
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<tr>
<td>#5</td>
<td>0.82</td>
<td>2.34</td>
<td>0.51</td>
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</table>
Figure C.1 Chloride Vaporization as a function of BL Chloride Content

Figure C.2 Potassium Vaporization as a function of BL Potassium Content
Figure C.3 Inorganic Component Balance Closures: Liquor to Liquor Study

Figure C.4 Black Liquor Solids Carbonate Estimates and Ion Balances
Figure C.5 Char Carbonate Estimates and Ion Balances

Figure C.6 Fume Carbonate Estimates and Ion Balances
APPENDIX D.

LIQUOR TO LIQUOR STUDY DATA
Table D.1 Liquor to Liquor Study Data

<table>
<thead>
<tr>
<th>Collector Position</th>
<th>Liquor Source</th>
<th>Liquor #1</th>
<th>Liquor #2</th>
<th>Liquor #3</th>
<th>Liquor #4</th>
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<td>19.2</td>
<td>20</td>
<td>20.5</td>
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</table>

**Note:**
1. Data groups in *italics* were used for chemical analysis of liquor, char, and fume.
2. Liquor #3 flow, fume, and char data is regression predicted from all of the liquor #3 runs.
APPENDIX E.

CALCULATIONS
E.1 Liquor Feed Rate Study Calculations

Oxygen requirement calculations for liquor #3.

Assumptions:

1. BL Elemental Analysis: 20% Na, 4% S, 37% C, 4% H, 35% O

2. \[ 2Na + S \rightarrow Na_2S \]
\[ 2Na + C + \frac{3}{2}O_2 \rightarrow Na_2CO_3 \]
\[ C + O_2 \rightarrow CO_2 \]
\[ H + H + \frac{1}{2}O_2 \rightarrow H_2O \]

Taking 1 gram of black liquor as a basis, we have: 0.20g Na/g BL, 0.04g S/g BL, 0.37 g C/g BL, 0.04g H/g BL, 0.35 g O/g BL.

Sodium:
\[ \frac{0.20 \text{ g Na}}{\text{g BL}} \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} = 0.00870 \frac{\text{mol Na}}{\text{g BL}} \]

Sulfur:
\[ \frac{0.04 \text{ g S}}{\text{g BL}} \times \frac{1 \text{ mol S}}{32.07 \text{ g S}} = 0.001247 \frac{\text{mol S}}{\text{g BL}} \]

Carbon:
\[ \frac{0.37 \text{ g C}}{\text{g BL}} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 0.03081 \frac{\text{mol C}}{\text{g BL}} \]

Hydrogen:
\[ \frac{0.04 \text{ g H}}{\text{g BL}} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 0.03968 \frac{\text{mol H}}{\text{g BL}} \]

Oxygen:
\[ \frac{0.35 \text{ g O}}{\text{g BL}} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.02188 \frac{\text{mol O}}{\text{g BL}} \]

Sodium available for carbonation:
\[ \frac{0.001247 \text{ mol S}}{\text{g BL}} \times \frac{2 \text{ mol Na}}{1 \text{ mol S}} = 0.002494 \frac{\text{mol Na}}{\text{g BL}} \]
Na for carbonation: \[
\frac{0.0087 \text{ mol Na}}{\text{g BL}} - \frac{0.002494 \text{ mol Na}}{\text{g BL}} = 0.006205 \frac{\text{mol Na}}{\text{g BL}}
\]

Carbon available for combustion:
\[
\frac{0.006205 \text{ mol Na}}{\text{g BL}} \times \frac{1 \text{ mol C}}{2 \text{ mol Na}} = 0.003103 \frac{\text{mol C}}{\text{g BL}}
\]

C for combustion:
\[
\frac{0.03081 \text{ mol C}}{\text{g BL}} - \frac{0.003103 \text{ mol C}}{\text{g BL}} = 0.0277 \frac{\text{mol C}}{\text{g BL}}
\]

Oxygen required for complete combustion
\[
\frac{0.0277 \text{ mol C}}{\text{g BL}} \times \frac{1 \text{ mol } O_2}{1 \text{ mol C}} = 0.0277 \frac{\text{mol } O_2}{\text{g BL}} \quad \sum = 0.03762 \frac{\text{mol } O_2}{\text{g BL}}
\]

\[
\frac{0.03968 \text{ mol H}}{\text{g BL}} \times \frac{1 \text{ mol } O_2}{2 \text{ mol H}} = 0.0099 \frac{\text{mol } O_2}{\text{g BL}}
\]

Correction for oxygen in black liquor
\[
\frac{0.02188 \text{ mol O}}{\text{g BL}} \times \frac{1 \text{ mol } O_2}{2 \text{ mol O}} = 0.01094 \frac{\text{mol } O_2}{\text{g BL}}
\]

\[
\frac{0.03762 \text{ mol } O_2}{\text{g BL}} - 0.01094 \frac{\text{mol } O_2}{\text{g BL}} = 0.0267 \frac{\text{mol } O_2}{\text{g BL}}
\]

All experiments were performed using an oxygen flow of 0.800 standard liters/min.
O₂ Feed Rate: \[ n = \frac{\frac{1 \text{ atm} \times 0.800 \text{l}}{0.08206 \text{ l} \cdot \text{atm} \cdot 273 \text{K}}}{\text{min}} = 0.03571 \text{ mol O}_2 \text{ min}^{-1} \]

Calculations for error estimation of fume experiments

For a 95% confidence interval, \( 1 - \alpha = 0.95 \), \( \alpha = 0.05 \), \( \alpha/2 = 0.025 \),

From the standard normal distribution, \( Z_{\alpha/2} = Z_{0.025} = 1.963 \)

95% confidence interval = sample mean +/- 1.963*\( \sigma/\sqrt{n} \)

**E.2 Calculations of Sodium Partial Pressure**

Using liquor #5 for example,

- Black liquor solids feed rate: 0.73 g/min
- Fume (% of BL solids): 16.7%
- Mass fraction Na in fume: 0.334
- Total gas flow (primary + secondary): 20 l/min

Total Molar Flow of Gas Entering Collector:

Molar Flow of Gases Fed to Reactor (at STP):

\[
\dot{N}_{\text{feed}} = \frac{\dot{V}P}{RT} = \frac{20 l \cdot 1 \text{ atm} \cdot \text{Pa}}{\text{min} \cdot 0.08206 \text{ l} \cdot \text{atm} \cdot 273 \text{K}} = 0.893 \text{ mol gas min}^{-1}
\]

Molar flow of Gases Produced During Combustion of Carbon:

Assumptions:

1. Liquor Composition: 20% Na, 4% S, 37% C, 4% H, 35% O
2. Reactions: See Excess Air Calculations
3. 100% of Carbon is Oxidized to CO₂

\[ N_C = \frac{0.0277 \text{ mol C}}{g \ BL} \]

\[ \dot{N}_C = \frac{0.0277 \text{ mol C} \times 0.73 \text{ g BL}}{g \ BL \text{ min}} = \frac{0.0202 \text{ mol C}}{\text{min}} \]

\[ \dot{N}_{CO_2} = \frac{0.0202 \text{ mol C} \times 1 \text{ mol CO}_2}{1 \text{ mol C} \text{ min}} = \frac{0.0202 \text{ mol CO}_2}{\text{min}} \]

Molar flow of Sodium Vaporized:

\[ \dot{N}_{Na(v)} = \frac{0.73 \text{ g BL} \times 0.167 \text{ g Fume} \times 0.334 \text{ g Na} \times 1 \text{ mol Na}}{22.99 \text{ g Na} \text{ min}} = \frac{0.00177 \text{ mol Na(v)}}{\text{min}} \]

Total Molar Flow of Gas Entering Collector:

\[ (0.863 + 0.0202 + 0.00177) = \frac{0.914 \text{ mol gas}}{\text{min}} \]

Mole Fraction of Na in the Vapor Phase:

\[ y_{Na(v)} = \frac{0.00177}{0.914} = 0.00193 \]

According to the model of Wåg, at 1000°C, \( y_{Na(v)} \sim 0.012 \) at equilibrium.

Experimental conditions are at 0.00193/0.012 = 16.1% of that predicted by model

E.3 Ion Balance Calculations

Anions: Cl⁻, SO₄²⁻, SO₃²⁻, S₂O₃²⁻, Balance CO₃²⁻

Cations: Na⁺, K⁺
Example Calculation with fume produced from liquor #3:

\[
CT = \frac{\text{mol}}{35.45 \text{ g mol}} \times \frac{1 \text{ eq}}{\text{mol}} = 0.02821 \text{ eq Cl}^-
\]

\[
\text{SO}_4^{2-} = \frac{\text{mol}}{96.07 \text{ g mol}} \times \frac{2 \text{ eq}}{\text{mol}} = 0.020818 \text{ eq SO}_4^{2-}
\]

\[
\text{SO}_3^{2-} = \frac{\text{mol}}{80.07 \text{ g mol}} \times \frac{2 \text{ eq}}{\text{mol}} = 0.02498 \text{ eq SO}_3^{2-}
\]

\[
\text{S}_2\text{O}_3^{2-} = \frac{\text{mol}}{112.14 \text{ g mol}} \times \frac{2 \text{ eq}}{\text{mol}} = 0.01783 \text{ eq S}_2\text{O}_3^{2-}
\]

\[
\text{CO}_3^{2-} = \frac{\text{mol}}{60.07 \text{ g mol}} \times \frac{2 \text{ eq}}{\text{mol}} = 0.0333 \text{ eq CO}_3^{2-}
\]

\[
\text{Na}^+ = \frac{\text{mol}}{22.99 \text{ g mol}} \times \frac{1 \text{ eq}}{\text{mol}} = 0.043497 \text{ eq Na}^+
\]

\[
\text{K}^+ = \frac{\text{mol}}{39.10 \text{ g mol}} \times \frac{1 \text{ eq}}{\text{mol}} = 0.025575 \text{ eq K}^+
\]

Sum EQ Cations = 0.354*0.043497 + 0.0361*0.025575 = 0.01632 eq (+)

Sum EQ Anions = 0.0929*0.02821 + 0.16*0.020818 + 0.0025*0.02498 + 0.0007*0.01783 + X eq CO\text{3}^{2-} = 0.00603 eq (-) + X eq CO\text{3}^{2-}

Charge Balance: Cations = Anions

0.01632 eq (+) = 0.00603 eq (-) + X eq CO\text{3}^{2-}

X eq CO\text{3}^{2-} = 0.01029 eq CO\text{3}^{2-}

Carbonate Estimate (mass %) = 100 * \frac{0.01029 \text{ eq CO}_3^{2-} * 60.01 \text{ g CO}_3^{2-}}{2 \text{ eq CO}_3^{2-}} = 30.9%
** Note that the carbonate estimate is expressing the balance of anionic equivalents (which contains both sodium carbonate as well as other organic anionic constituents) as the balance of anions.

E.4 Calculations Estimating Oxygen Transport From Bulk Gas to Particle Cloud at LEFR Axis

Velocity Profile Calculations

Assumptions:

1. Laminar Flow
2. Incompressible Flow
3. \( V_r \sim 0, V_\theta \sim 0 \)
4. Steady State \( \frac{\partial (\cdot)}{\partial t} \approx 0 \)

\[
\rho \left( \frac{\partial \tau_{r,z}}{\partial t} + v_r \frac{\partial \tau_{r,z}}{\partial r} + v_\theta \frac{\partial \tau_{r,z}}{\partial \theta} + v_z \frac{\partial \tau_{r,z}}{\partial z} \right) = -\frac{\partial P}{\partial z} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \tau_{r,z} \right) + \frac{1}{r} \frac{\partial}{\partial \theta} \left( \tau_{r,z} \right) + \frac{\partial}{\partial z} \tau_{r,z} \right) + \rho g_z
\]

\[
0 = -\frac{\partial P}{\partial z} - \frac{1}{r} \frac{\partial}{\partial r} \left( r \tau_{r,z} \right) + \rho g_z
\]

\[
\frac{1}{r} \frac{d}{dr} \left( r \tau_{r,z} \right) = \rho g_z - \left( \frac{P_L - P_0}{L - 0} \right)
\]

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \tau_{r,z} \right) = \rho g_z - \frac{\partial P}{\partial z}
\]
Figure E.1 Profiles within the Laminar Entrained Flow Reactor

\[ \int d(r \tau_{r,z}) = \int r \left( \frac{P_0 - P_L}{L} + \rho g \right) dr \]

\[ \tau_{r,z} = \frac{r}{2} \left( \frac{P_0 - P_L}{L} + \rho g \right) + \frac{C_1}{r} \]

BC1: \( \tau_{r,z} \neq \infty \) at \( r=0 \), \( C_1 = 0 \)

\[ \tau_{r,z} = -\mu \frac{dv_{z}}{dr} \]

\[ -\mu \frac{dv_{z}}{dr} = \frac{r}{2} \left( \frac{P_0 - P_L}{L} + \rho g \right) \]
\[
\int dv_z = -\int \frac{r}{2\mu} \left( \frac{P_0 - P_L}{L} + \rho g \right) dr
\]

\[v_z = -\frac{r^2}{4\mu} \left( \frac{P_0 - P_L}{L} + \rho g \right) + c_2\]

BC2: \( v_z = 0 \) at \( r = R \),

\[c_2 = \frac{R^2}{4\mu} \left( \frac{P_0 - P_L}{L} + \rho g \right)\]

\[v_z = \left( \frac{P_0 - P_L}{L} + \rho g \right) \left( \frac{R^2 - r^2}{4\mu} \right)\]

\[v_z = \frac{R^2}{4\mu} \left( \frac{P_0 - P_L}{L} + \rho g \right) \left( 1 - \frac{r^2}{R^2} \right)\]

\[v_z = \frac{R^2}{4\mu} \left( \frac{P_0 - P_L}{L} + \rho g \right) \left( 1 - \left( \frac{r}{R} \right)^2 \right)\]

**E.5 Mass Transfer Calculations**

Assumptions:

1. \( \text{O}_2 \) diffuses to the particle column through laminar flow

2. Neglect convection effects, assume \( \text{O}_2-\text{N}_2 \) system

3. Neglect temperature gradients, assume \( T=1000^\circ\text{C} \)

4. Neglect heat of reaction

5. Assume fully developed laminar flow
6. Reaction immediately consumes O₂ at particle column near axis of LEFR

7. Steady State \( \frac{\partial()}{\partial t} \approx 0 \)

\[
D_1 \left( \frac{\partial^2 C_1}{\partial r^2} + \frac{1}{r} \frac{\partial C_1}{\partial r} + \frac{1}{r^2} \frac{\partial^2 C_1}{\partial \theta^2} + \frac{\partial^2 C_1}{\partial z^2} \right) - \left( v_r \frac{\partial C_1}{\partial r} + v_\theta \frac{\partial C_1}{\partial \theta} + v_z \frac{\partial C_1}{\partial z} \right) + B_1 = \frac{\partial C_1}{\partial t}
\]

\[
D_1 \left( \frac{\partial^2 C_1}{\partial r^2} + \frac{1}{r} \frac{\partial C_1}{\partial r} + \frac{\partial^2 C_1}{\partial z^2} \right) - v_z \frac{\partial C_1}{\partial z} = 0
\]

BC1: at \( z=0, \ r=R_C \); \( C_1 = 0 \)

BC2: at \( z=0, \ r=R \); \( C_1 = Y_1(P/RT) \)

BC3: at \( z=L, \ r=R_C \); \( C_1 = 0 \)

Inadequate boundary conditions to describe physical situation
### E.6 Fume Analysis of Variance (ANOVA)

Liquor #1 | Liquor #4 | Liquor #5 | Liquor #2 | Liquor #3
---|---|---|---|---
14.6 | 15.6 | 16.1 | 13.8 | 17
15.3 | 16.5 | 16.7 | 14.9 | 16.8
14.2 | 14 | 17.2 | 16.5 | 16.7

Anova: Single Factor  \( \alpha = 0.05 \) Significance Level

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Anova: Single Factor  \( \alpha = 0.0355 \) Significance Level

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**E.7 Char Analysis of Variance (ANOVA)**

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**Anova: Single Factor**  
Alpha = 0.05 Significance Level

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**ANOVA**

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Anova: Single Factor  
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