45 YEARS RECOVERY BOILER CO-OPERATION IN FINLAND

PROCEEDINGS
45th ANNIVERSARY INTERNATIONAL
RECOVERY BOILER CONFERENCE

Sibelius Hall, Lahti, June 3 – 5, 2009

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Cover photos:
Scenery of new recovery boiler at UPM-Kymmene Oyj, Kymi, Kuusankoski
Sibelius Hall, Lahti
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YEAR 2009 will be remembered for two reasons. Firstly, 2009 will probably be one of the most difficult years in the history of the pulping industry. Hard times are globally present and several pulp mills have been permanently closed. All the companies have experienced diminished revenues and have begun cost-cutting measures. Secondly, year 2009 will mark the 45th year for the activities of the Finnish Recovery Boiler Committee. To celebrate the occasion this International seminar has been arranged in Lahti, Finland.

The Finnish Recovery Boiler Committee has also seen the effects of the global decline. Three pulp mills have recently been permanently shut down in Finland, which means that the committee has also lost three active members. However, the bad news always comes with the good news. One of the recent good news is definitely the start-up of a brand new recovery line at the UPM-Kymmene Kuusankoski mill in 2008. The investment in a new recovery line proves that pulp will be produced in Finland also in the future.

The Finnish Recovery Boiler Committee has also been active in promoting safe, economic and environmentally friendly operation of recovery boilers and closely related processes. The Committee publishes different guidelines, recommends best practices and arranges meetings and conferences. Most of the active work is done in five subcommittees, which cover the most important areas around the recovery boiler.

During the recent years, the Finnish Recovery Boiler Committee has taken a more active role to manage large research projects. The first major publicly funded project (SOTU 2) was started in 2003. The Finnish Funding Agency for Technology and Innovation (Tekes) was the main financier of the project. The SOTU 2-project was a big effort to the Committee, but it became a great success. SOTU 2 concentrated mainly on the possibilities to increase power production from the recovery boilers. Another major Tekes-funded project (SKYREC) started in the first quarter of 2008. This project will further deepen the understanding needed in the design and operation of the high-efficiency recovery boilers in the future. SKYREC-project is now in a good pace and has also raised a lot of international interest toward the Finnish Recovery Boiler Committee and its activities.

The pulping industry has faced both lows and highs in the course of history, but has always survived. One of the main functions of the Finnish Recovery Boiler Committee is to distribute knowledge of recovery equipment and operation, which will help the industry to develop highly efficient production units with high availability.

Despite this transient decline, I hope we all look ahead and have a strong faith in future. At least the Finnish Recovery Boiler Committee believes on a prosperous and active future. With these words I’d like to congratulate the Recovery Boiler Committee of its 45 year milestone and welcome you all to this anniversary conference.
Introduction

Pulp mills and recovery boilers are becoming larger and larger. From humble beginnings the recovery boiler now reaches for the title of largest biomass fired boiler in the world. Globally the pulp and paper industry is in recession. But several new large mills are being built around the world. Even larger mills are in the works.

New expectations have been imposed on chemical recovery department operations. Cutting down air emissions is not enough. Pulp and paper mills need to maximize their bioenergy potential and minimize their electricity consumption to produce green electricity for sale outside the mill.

Recovery boilers, which have always produced bioenergy, have evolved significantly in the past 70 years. For pulp mills the significance of electricity generation from the recovery boiler has historically been secondary. The most important design criterion for the recovery boiler has been high availability. This evolution has culminated with units that are among the largest biofuel boilers in the world. Currently the focus is shifting towards more challenging designs that maximize electricity production.

From old to new

“There is no stopping for progress” applies also to recovery boilers. The recovery departments built today are bigger, more efficient and geared to produce more electricity than ever. This can be easily seen when we compare the first recovery boilers to last recovery boiler started in Finland at UPM-Kymmene Kymi mill in May 2008.

First Recovery Boilers

The modern recovery boiler has a few strong ideas that have remained unchanged until today. It was the first recovery equipment type where all processes occurred in a single vessel. The drying, combustion and subsequent reactions of black liquor all occur inside a cooled furnace. This is the main idea in Tomlinson’s work.

Secondly the combustion is aided by spraying the black liquor into small droplets. Controlling process by directing spray proved easy. Spraying was used in early rotary furnaces and with some success adapted to stationary furnace by H. K. Moore. Thirdly one can control the char bed by having primary air level at char bed surface and more levels above. Multiple level air system was introduced by C. L. Wagner.

Figure 1. First Tomlinson kraft recovery boiler from Babcock & Wilcox in 1929 [1].
Recovery boiler also improved the smelt removal. It is removed directly from the furnace through smelt spouts into a dissolving tank. Some of the first recovery units employed the use of Cottrell’s electrostatic precipitator for dust recovery.

Babcock & Wilcox was founded in 1867 and gained early fame with its water tube boilers. It built and put into service the first black liquor recovery boiler in the world in 1929 [1]. This was soon followed by a unit with completely water cooled furnace at Windsor Mills in 1934. After reverberatory and rotating furnaces the recovery boiler was on its way.[2]

The second early pioneer, Combustion Engineering based its recovery boiler design on the pioneering work of William M. Cary, who in 1926 designed three furnaces to operate with direct liquor spraying and on work by Adolph W. Waern and his recovery units. Recovery boiler were soon licensed and produced in Scandinavia and Japan. These boilers were built by local manufacturers from drawings and with instructions from licensors. One of the early Scandinavian Tomlinson units employed a 8.0 m high furnace that had 2.8*4.1 m furnace bottom which expanded to 4.0*4.1 m at superheater entrance [3]. This unit stopped production for every weekend. In the beginning economizers had to be water washed twice every day, but after installation of shot sootblowing in the late 1940s the economizers could be cleaned at the regular weekend stop. The construction utilized was very successful. The 160 t/day unit at Korsnäs operated still almost 50 years later.[4] Edling [5] states in 1937 that more than 20 units had already been built of which 10 in Scandinavia.

**Newest capacity**

The current recovery boiler, Figure 2, can be much larger than the previous ones. Boilers with over 200 square meter bottom area have been bought. Largest recovery boilers are challenging circulating fluidized boilers for the title of largest bio-fuel fired boiler.

The superheater arrangement is designed for optimum heat transfer with extra protection to furnace radiation. Mill closure and decreased emissions mean higher chloride and potassium contents in black liquor. Almost all superheaters are placed behind the bullnose to minimize the direct radiative heat transfer from the furnace. Increasing superheating demand with increasing pressure decreases the need for boiler bank and water screen arrangement.

The higher main steam outlet temperature requires more heat to be added in the superheating section. Therefore the furnace outlet gas temperature has increased. The alternative is to significantly increase superheating surface and decrease boiler bank inlet flue gas. If boiler bank inlet gas temperature is reduced the average temperature difference between flue gas and steam is also decreased. This reduces heat transfer and substantially more superheating surface is needed. This approach has been abandoned because of increased cost. With increasing dry solids content the furnace exit temperature can safely increase without fear of corrosion caused by carryover.

**New capacity development**

Figure 3 shows the firing capacity of over 1000 recovery boilers that have been built in the world to date.[10] This capacity has grown about 3 % per year since 1970 when the maximum was 2041 tds/d. If this rate goes on, then the first 10 000 tds/d recovery boiler will start operating in 2024. Finnish Recovery Boiler Committee will then celebrate its 60th operating year.
Current black liquor processing capacity in Finland is about 40 000 tds/d. Finnish Recovery Boiler Committee will celebrate its 100th operating year in 2064. Hopefully we can then show again a new big recovery boiler. This boiler will be able to process all black liquor in Finland. The furnace loading for new boilers is now at 3400 kW/m² and is growing about 20 kW/m² per year. So the furnace loadings will be 3700 kW/m² and 4500 kW/m² respectively for 2024 and 2064. If the black liquor design HHV of 14 MJ/kgds will remain unchanged, then the new boilers will have bottom areas of 440 and 1200 m² respectively for 2024 and 2064. The corresponding furnace dimensions will be 21*21*52 m and 34*35*79 m.

In the last ten years (1999 – 2008) about one third of the installed capacity has been at green field mills. Most of the new recovery projects are at established sites, which offer much more competitive infrastructure. New recovery capacity is built especially in Asia and South-America, where pulp production capacity is strongly expanding, Figure 4. Europe and North-America account for less than half of total new recovery capacity. We are facing an era where hardwood based pulp mills are favored over softwood pulp mills. About half of new mills are built to produce eucalyptus pulp. Recovery departments of eucalyptus mills are now an established technology [11].

A lot of the North-American and European recov-

Table 1. Comparison of early Scandinavian boiler with Kymi boiler.

<table>
<thead>
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<th></th>
<th>Early Scandinavia[?]</th>
<th>Kymi[8,9]</th>
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<tbody>
<tr>
<td>Capacity</td>
<td>tds/d</td>
<td>160</td>
</tr>
<tr>
<td>Steam generation</td>
<td>kg/s</td>
<td>7</td>
</tr>
<tr>
<td>Steam pressure</td>
<td>MPa(a)</td>
<td>35</td>
</tr>
<tr>
<td>Steam temperature</td>
<td>°C</td>
<td>370</td>
</tr>
<tr>
<td>Furnace height</td>
<td>m</td>
<td>8</td>
</tr>
<tr>
<td>Furnace bottom area</td>
<td>m²</td>
<td>11.5</td>
</tr>
<tr>
<td>Boiler house height</td>
<td>m</td>
<td>17</td>
</tr>
</tbody>
</table>

Figure 3. Black liquor firing capacity of recovery boilers built in the world versus their years of start-up.[10]
ery capacity is old. Average boiler age is about 30 years, Figure 3. Recovery boiler technical life expectancy is around 30 - 40 years [12]. This means that in USA and Sweden within next ten years investment in older mills is needed. The alternative is the continuing closure of pulp mills. If we assume the age distribution to be the same then about 50 % of the recovery boiler capacity in USA and Sweden need to be rebuilt by 2024. By 2064 none of the current recovery boilers are in use, but black liquor gasification will possibly still be 10 years from realization.

**Higher black liquor dry solids**
The modern kraft recovery process is the result of decades of continued small improvements of the basic technology. One important development in recovery boiler operation is “high-solids firing” which refers to burning black liquor at solids contents greater than 75%. The practice significantly increases steam generation and improves combustion stability, resulting in lower TRS and SO₂ emissions, and less boiler fouling and plugging. It also provides for more capacity in existing units. In Scandinavia the new units are currently purchased based on 85% dry solids content at as-fired liquor.

![Figure 4. New recovery capacity by region 1999 - 2008.](image)

![Figure 5. Age of recovery boilers in USA, Sweden, Finland and Brazil.](image)
Maximum black liquor dry solids content has always been limited by the ability of available evaporation technology to handle the highly viscous concentrated liquor. As evaporator technology has evolved, the final black liquor dry solids content has increased. Dry solids content of virgin black liquor (without ash recycle) is shown in Figure 6 as a function of start-up year of the boiler.

When looking at the virgin black liquor dry solids we note that on average dry solids content has increased. This is especially true for latest very large recovery boilers. Design dry solids for green field mills have been either 80 or 85 % dry solids. 80 % dry solids have been in use in Asia and South America (hardwood liquors). 85 % has been in use in e.g. Finland (softwood liquors).

The maximum black liquor content has increased by about 10 percentage points in about 30 years. 2004 was the year when first new evaporators were bought for 85 % dry solids. If this trend continues, then when Finnish Recovery Boiler Committee will celebrate its 60th operating year in 2024 the black liquor is respectable 95 % dry solids. Black liquor will be totally dry (100 % dry solids) in 40 years (2049). When Finnish Recovery Boiler Committee will celebrate its 100th operating year in 2064 the black liquor is 105 % dry solids. The first stage of combustion of black liquor will then consist of black liquor droplet drawing water vapor from surroundings. This kind of behavior will necessitate new combustion and firing research.

The amount of power a recovery boiler can generate from black liquor combustion depends on the pressure and temperature of the steam that the boiler produces. Traditionally, recovery boilers have operated at moderate steam pressures (≤80 bar) and temperatures (≤480 °C) due to concerns over superheater corrosion and high costs of materials for construction. Of the last 20 recovery boilers about 80 % have chosen higher pressures and temperatures. Some have done this without resorting to more expensive materials. Today there is a number of recovery boilers operating at >100 bar and >500°C. The lead in these developments has been taken in Japan [13,14] and Scandinavia [15,16]. But high efficiency boilers are now being built also in North and South America. Because of corrosion issues potassium and chlorine removal equipment are definitely needed especially in high pressure and temperature applications.

**Modern recovery boiler**

The state-of-the-art recovery boiler is much larger than the previous designs. Boilers with over 250 square meter hearth area have been bought. The largest recovery boilers are challenging circulating fluidized bed boilers for the title of largest biofuel fired steam generators in the world.

The largest operating recovery boiler in the world is presently the Metso Power unit started up in November 2004 at the Jinhai Pulp & Paper mill in Hainan, China, Figure 7. The unit has a furnace floor area of 268 m², a nominal firing capacity of 5000 tds/d (6000 tds/d maximum) and can produce 204 kg/s steam rated at 84 bar and 480°C [19].

![Figure 6. Virgin black liquor dry solids as a function of start-up year of the recovery boiler.](image-url)
Recovery boiler design changes slowly. There are however some features that the boilers bought today have in common. The state of the art recovery boiler design will be that of a single drum, high solids firing unit with multiple levels of air supplied by separate fans, as shown in Figure 7. It will have a greater superheater surface area and be equipped with feedwater preheaters and/or combustion air preheaters in order to produce high-pressure/temperature steam. In some units the combustion air temperature is up to 190 °C and feedwater tank operates close to low pressure steam temperature. Many new greenfield pulp mills are equipped with a multiple extraction back pressure turbine combined with a condensing turbine to maximize power generation. A recent new feature is heat recovery after the electrostatic precipitators [20].

The recovery boiler has adopted a position of waste destruction unit. What can be destroyed by burning will likely be burned in it. Half of the new boilers are burning sludge from biological effluent treatment and some even filtrate from bark presses. Almost all new boilers burn weak NCG gases and dissolving tank vent gases. A majority of new units burn strong NCG gases with a dedicated burner in the furnace.
The state-of-the-art recovery boiler is environmentally friendly. It has multiple air levels above the liquor gun level for efficient NO\textsubscript{x} control. Low emissions of TRS and SO\textsubscript{2} with NCG firing are typically achieved. The trend has been to decrease the particulate emission by applying larger and more efficient electrostatic precipitators. Use of scrubbers to recover heat is becoming rare.

Sootblowers, which are used to control the accumulation of deposits on tube surfaces in recovery boilers, will be equipped with fully-expanded nozzles, variable lance speeds and intelligent sootblowing systems to maximize deposit removal efficiency while minimizing sootblowing steam usage. It remains to be seen whether the new recovery boilers will use low pressure steam after the steam turbine (10 to 15 bars) for sootblowing [21], instead of the conventional high pressure steam (20 to 24 bars).

### Changing recovery boiler main parameters

Main design parameters of the recovery boiler affect the steam and electricity generation. Significantly more power generation can be achieved if higher main steam pressure and temperature are chosen. Average main parameters of new recovery capacity by region 1997 - 2006 are shown in Table 2.

The trend in recent years has been definitely in favor of increased temperatures and pressures. Newest Scandinavian and North-American lines, have chosen main steam values in excess of 80 bar and 480 °C [22,23] and Table 2. It can be seen that in e.g. China and Indonesia there is still resistance to high main steam parameters. This is understandable when opportunities to sell excess electricity do not yet exist.

### Table 2. Average main parameters of new recovery capacity by region 1999 – 2008.

<table>
<thead>
<tr>
<th>Region</th>
<th>Capacity tds/d</th>
<th>Steam temp. °C</th>
<th>Steam press. bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Africa</td>
<td>630</td>
<td>472</td>
<td>78</td>
</tr>
<tr>
<td>Asia</td>
<td>2720</td>
<td>474</td>
<td>78</td>
</tr>
<tr>
<td>Europe</td>
<td>2350</td>
<td>487</td>
<td>88</td>
</tr>
<tr>
<td>North-America</td>
<td>1780</td>
<td>488</td>
<td>90</td>
</tr>
<tr>
<td>Oceania</td>
<td>670</td>
<td>460</td>
<td>64</td>
</tr>
<tr>
<td>South-America</td>
<td>2460</td>
<td>480</td>
<td>84</td>
</tr>
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### Figure 9. Development of recovery boiler main steam temperature.

[Graph showing the development of recovery boiler main steam temperature from 1937 to 2012.]

[Table showing average main parameters of new recovery capacity by region 1999 – 2008.]

[Diagram showing the development of recovery boiler main steam temperature.]
The maximum and average steam temperatures have increased, Figure 9. The average steam temperature is now about 480 °C (Figure 9 and Table 2). The average steam temperature has increased about 1.5 °C per year. By 2024 the average steam temperature will be over 500 °C. The conservative steam temperature 540 °C used in PCF boilers will be reached by 2049. This further confirms that technologically recovery boilers are 30 - 40 lagging the power boilers. Steam pressure needs to correspond to steam temperature. The high end of recovery boilers uses pressures of about 90 bar (Figure 10 and Table 2). The average steam pressure has increased about 0.8 °C per year. By 2024 the average main steam pressure will be over 110 bar. The maximum usable natural circulation pressure will be reached by 2049. So after just 40 years the recovery boilers need to be of once-through design. The steam temperatures are limited by the ash properties. So either new materials are needed or the ash chemistry needs to be redesigned with high temperatures in mind.

**Future trends and challenges**

Back liquor gasification still struggles to be acknowledged as a potential replacement for recovery boilers. The driving force for these alternative recovery technology developments has been the potential for much greater electricity production. New high efficiency recovery boilers have considerably reduced this gap. As many material and gas cleanup issues remain to be resolved, the first large-scale gasification plant still appears to be years away.

Attention is now shifting to using black liquor gasification to produce synthesis gas as a raw material for making higher value chemicals for sale. This is sometimes referred to as the biorefinery concept. It is more probable that plants using direct biomass gasification will reach wide commercialization first. In any case integration of these plants to pulp mills will provide new challenges and opportunities.

The recovery boiler, as a producer of green energy, requires new materials and attention to feedwater quality. The role of chlorine and potassium removal in preventing superheater corrosion must be established. The recovery rating should be changed to tons of assayed black liquor because virgin black liquor is a non measurable quantity in modern installations (due to complex recycling arrangements).

**Conclusions**

New recovery capacity is being built at considerable pace. Large number of recovery boilers in North America and Sweden are approaching the end of their technical lifetime. If we are to reverse the trend of pulp mill closure in North America, further investment to recovery is needed.

The size of equipment in newest recovery departments continues to grow. Recovery boiler capacity has surpassed 6000 tds/d (13 million lb ds/day).

The main future challenge is to respond to changing business environment. Closer integration with biofuels production, higher bioelectricity production and less CO₂ production are just few of the changes required.
References
Introduction

Black Liquor Recovery Furnace is one of the most complex large scale industrial reactors around. On one hand it takes care of recovery of the cooking chemicals sodium and sulfur in a chemically suitable form – as a mixture of alkali carbonate and sulfide – to be tapped from the furnace floor as a smelt. On the other hand it is a reactor for clean combustion of the organic part of the liquor to generate heat and power in a steam boiler cycle.

Black liquor recovery furnace processes are complex, but systematic research has improved our understanding of these processes considerably. Different approaches have been applied to learn more about the recovery boiler. Various types of measurements are carried out in operating boilers to explore the state and composition of the fuel gases in different parts of the furnace. Ingenious laboratory measurements have given valuable information of the details of the properties and behavior of burning liquor droplets, chemical reactions in the furnace gases etc.

Mathematical modeling based on CFD has become an excellent tool to really test our overall understanding of the furnace processes. The CFD-based model gives us a possibility to combine our detailed understanding of the many furnace phenomena into an overall description of the behavior of a full scale furnace.

CFD has been applied to recovery boilers for nearly two decades. CFD is originally a general methodology for modeling fluid flow. Therefore, application of it to study air systems and gas flows inside the recovery furnace was a natural early development. More efficient computers, user-friendly programs, and more detailed models have contributed to the increased use of CFD in more comprehensive studies of recovery boilers.

This paper discusses some of the recent advances in the CFD-based modeling of recovery furnaces. The emphasis is on some special features of the black liquor recovery furnace as compared with conventional furnaces in which CFD based modeling has been applied. While the material presented focuses mainly on the modeling carried out at Åbo Akademi, significant modeling research in other laboratories is carried out [1-7].

There are many physical and chemical phenomena which need to be described in CFD-based modeling of recovery boilers. Many of these phenomena are similar to other types of combustion furnaces, and can be directly applied to recovery boilers as well. These include the turbulent gas flow, radiative and convective heat transfer, particle flight in the gas flow etc. For black liquor, the most important specific submodels include description of the liquor droplet conversion, some chemical reactions in the gas phase, and the process of the char bed formation and oxidation. The models interact with each other, meaning that as the droplets fly inside the furnace they exchange energy and mass with the gas phase, and the products from droplet conversion react further in the gas phase. In addition, the material landing on the char bed and the local gas environment affect char bed burning.

Droplet Combustion Model - The Key to Furnace Modelling

Black liquor is a unique fuel: it contains large amounts of inorganic matter, its char is highly reactive due to the high loading of alkali, and its burning is connected with considerable swelling which varies from liquor to liquor. Laboratory studies using single droplets have provided insight into the combustion behavior of black liq-
Based on this knowledge, a general droplet burning model has been developed [10]. This droplet model can be made liquor specific by extracting information from laboratory experiments. It can then be used in full furnace simulations to study the effect of liquor-to-liquor differences on in-furnace combustion.

Such a study [10] was recently carried out by simulating combustion of two liquors: a High Swelling and a Low Swelling liquor. The liquors were burned in two recovery boilers: the boilers A and B. Some of the results of this study are presented in Figures 1-4. With the high swelling liquor, combustion takes place to a greater extent in-flight and higher up in the furnace as with the low swelling liquor. In addition, droplet combustion occurs in different regions of the two furnaces (Figures 3 and 4). The recovery boilers had considerably different capacities: 450 t DS/day and 3600 t DS/day, for A and B, respectively. In furnace B, the larger of the two, droplet combustion takes place to a greater extent in-flight.

Although there are uncertainties, these simulations show some of the positive aspects of CFD-based modeling. The first is data visualization, i.e., the results can be presented graphically as if we were looking into the furnace by using suitable colors to indicate e.g. temperature or composition of the furnace gases. This is a good way to get an overall picture of what takes place inside the recovery boiler. The second is that modeling gives data from within the furnace. The numerical information in Figures 3 and 4 could perhaps be estimated qualitatively, but would be impossible to extract from an operating recovery boiler by any experimental techniques.

In addition, the models are general and thus valid for any sizes of the furnaces. Thus, the impact of furnace size on the combustion inside it can be effectively studied. It is quite clear that the impressive increase in the size of the furnaces in the latest boiler deliveries would not have been possible without the support of CFD based modeling.

Figure 1, Influence of liquor swelling on temperature in Furnace A [10].
Figure 2, Influence of liquor swelling on temperature in Furnace B [10].

Figure 3, Influence of liquor swelling (Low Swelling Liquor LSL; High Swelling Liquor HSL) on the occurrence of the stages of combustion in different regions of Furnace A (in-flight F; on furnace wall W, on the char bed B [10].

Figure 4, Influence of liquor swelling (Low Swelling Liquor LSL; High Swelling Liquor HSL) on the occurrence of the stages of combustion in different regions of Furnace B (in-flight F; on furnace wall W, on the char bed B [10].
Nitrogen Oxides – Still a Challenge

Black liquor differs from all other fuels in its nitrogen chemistry. The special feature is that part of the organic nitrogen in the liquor after completed char oxidation may stay in the smelt residue as inorganic salt, sodium cyanate. This "smelt nitrogen" is a source of large amounts of nitrogen species – mostly ammonia – found in the various water solutions of the chemicals recovery cycle of the pulp mill. Today there is relatively good understanding of the fate of nitrogen in the recovery cycle (Figure 5) [11-15].

One main source of NO emissions from the recovery boiler is the part of the fuel nitrogen which is released during devolatilization [14,15]; an overview of the reactions of black liquor nitrogen is shown in Figure 6 [13,14]. The importance of the molecular nitrogen in the air as a source for NO (the so called thermal NO mechanism) is probably negligible (see below).

Modeling the NO formation in the recovery furnace requires a description of the release of the liquor nitrogen from the burning droplet. This can be made based on laboratory droplet burning studies. In the latest version of the droplet model [16], the following assumptions are included. As a first approximation it can be assumed that 30% of the nitrogen in the liquor goes to char; 35% is released as ammonia, NH₃; and another 35% as molecular nitrogen, N₂, during the devolatilization (or pyrolysis) stage of the droplet conversion. The release of ammonia can be assumed proportional to the rate of carbon released during pyrolysis. During char combustion of the droplets, nitrogen is assumed to be released as NO if the local environment is oxidizing, whereas no nitrogen is released if the conditions are reducing. The latter situation results in an increase in the N/C ratio in the char residue. If the final burnout of char carbon takes place under oxidizing conditions, the remaining nitrogen is released as NO.

Nitrogen chemistry in the gas phase is calculated using a reaction mechanism involving 21 species and 52 elementary reactions, including pathways also for thermal NO formation. Figure 7 presents simulated NO concentrations in a recovery furnace.

One of the findings of the study [16] was that thermal NO does not contribute to the NO emission from the recovery boiler. Although once again there are uncertainties, in this respect the simulation results are consistent with the current understanding of NO formation in recovery boilers. However, the models require further development to enable them to describe the full complexity of nitrogen chemistry in the recovery furnace.

Figure 5. Fate of nitrogen in the Kraft recovery cycle [11].
Figure 6. Overview of the reactions of black liquor nitrogen in the recovery furnace [13,14].

Figure 7. Simulated NO in a recovery furnace [16].
According to the simulations [16], the conditions in the furnace favor oxidation of \( \text{NH}_3 \) to NO. The amount of \( \text{NH}_3 \) released and the final NO at the furnace outlet matched almost perfectly, thus suggesting that essentially all \( \text{NH}_3 \) is oxidized to NO in the furnace process. The impact of droplet size on NO emissions from the furnace was investigated by varying the average droplet size in the black liquor spray. In the original coupled simulation of the furnace, an average droplet size of 6.3 mm was used. To avoid excessive computation time, the investigation of the impact of droplet size was carried out in post-processing mode: the velocity and temperature profiles in the furnace were frozen, and the impact of droplet size on these variables was neglected. Instead, for each average droplet size, the calculation of droplet trajectories took into account the release of nitrogen species from the droplets (Figure 8). In the droplet model, all volatile matter is released to the gas phase upon impact on a solid surface, i.e., the furnace walls or the char bed. For this reason, all volatile nitrogen is also released to the gas phase, Figure 8: the \( \text{NH}_3 \) release rate is independent of droplet size. However, nitrogen is released from droplets as NO only if char burnout takes place in-flight and under oxidizing conditions. The decrease in NO release from droplets with increasing droplet size (Figure 8) occurs because a higher share of droplets hit a furnace wall or the char bed before char burnout. This result suggests a decrease in the total NO emissions when liquor is sprayed into the furnace as larger droplets.

**Liquor Spraying – The Most Important Input**

Introduction of the fuel into the furnace as a relatively coarse spray is a special feature of black liquor combustion. Operational experience shows the furnace combustion process to be highly sensitive to differences in spraying. Extensive spray characterization has been carried out at the Helsinki University of Technology [17,18]. In addition, modeling of the actual droplet formation process in the liquor nozzle is ongoing [19]. However, such models are not yet available as submodels for a full simulation of the furnace. Therefore, in the meantime, the droplet formation process is neglected, and the black liquor spray is described in terms of droplet boundary conditions for direction, velocity, and mass flow rate.

These initial droplet parameters are essential for performing accurate furnace simulations, as was learned from a recent study on different spray models [20]. In this study three models were tested, whose features are illustrated in Figure 9. In the first model, droplets were introduced into the furnace using a small number of discrete injections; in the second, droplets were introduced into the furnace using a continuous distribution.

![Figure 8, Nitrogen release as a function of average droplet size [16].](image-url)
within a horizontal opening angle of 120°; and in the third, droplets were introduced into the furnace using a continuous distribution within both a horizontal (120°) and a vertical (10°) opening angle. The third model was included in the study because the spray characterization measurements carried out by Helsinki University of Technology showed that the liquor sheet formed at the liquor gun nozzle is not two-dimensional but in fact has a vertical opening angle. Some simulation results are presented in Figures 10 and 11.

Figure 9. Features of different spray models: 1) particles introduced in 11 discrete directions; 2) continuous distribution within a horizontal opening angle (120°); and 3) vertical opening angle (10°) also considered [20].

Figure 10. Furnace temperature distribution using three spray models: 1) particles introduced in 11 discrete directions; 2) continuous distribution within a horizontal opening angle (120°); and 3) vertical opening angle (10°) also considered [20].
Large droplets are not greatly influenced by turbulence inside the furnace. Therefore the in-flight combustion of these droplets is affected mainly by their boundary conditions at the wall, i.e., the spray model. The effect on furnace temperature is shown in Figure 10. The differences are best seen in the lower furnace. The main differences in the temperature fields are between the discrete injection model (Model 1) and models using continuous distributions within opening angles (Models 2 and 3). However, when both the horizontal and the vertical opening angle were considered (Model 3), the peak temperatures were higher up in the furnace than in Model 2, in which only the horizontal opening angle was considered.

The choice of spray model also influenced the droplet landing pattern on the char bed (Figure 11). Again the main difference is between continuous distributions (Models 2 and 3) and discrete injections (Model 1), but including the vertical opening angle (Model 3) resulted in more effective spreading of the droplets onto the bed. The droplet landing pattern is important for the simulation of bed shape, as will be shown later.

Char Bed – Can it also be Modelled?
The char bed is an additional special feature of black liquor recovery boilers. A model has been developed for describing char bed burning, including mechanisms for carbon conversion by oxygen, carbon dioxide, water vapor, and sulfate [21]. In this model carbon conversion, bed temperature, and net carbon accumulation are calculated locally based on mass and energy balances on the bed surface. The bed model is fully coupled with the droplets and gas phase above the bed. Thus, input of char carbon and inorganic salts is calculated from the droplets landing on the bed. In addition, the local gas velocity and composition affect carbon conversion. The model predicts the contribution of the various carbon conversion reactions involved in char bed burning. Some simulation results are presented in Figure 12 [21].

The carbon conversion rate seldom matches the rate of carbon input to the bed. Instead, net carbon accumulation is calculated as the difference between carbon arriving with droplets and carbon conversion; in other words, carbon can either accumulate or be depleted locally (Figure 13).

The net carbon accumulation can be interpreted as the parameter which determines the bed shape: the bed grows in areas where the net accumulation is positive, and bed depletion occurs in regions with negative net accumulation. Based on net carbon accumulation, changes in the char bed shape can be calculated as a function of time [22]. Starting from an initial shape, the bed shape is updated in small steps. For each new bed shape, the furnace model, including droplets, gas phase and the bed, is recalculated to obtain the new net carbon accumulation.

Figure 11, Droplet landing patterns on the char bed using three spray models: 1) particles introduced in 11 discrete directions; 2) continuous distribution within a horizontal opening angle (120°); and 3) vertical opening angle (10°) also considered [20].
Figure 12. Carbon conversion calculated using the char bed model coupled to a furnace simulation [21].

Figure 13. Net carbon accumulation calculated using the char bed model [21, 22].
The model was used to study the impact of the liquor spray initial droplet size on the bed shape [22]. Figure 14 presents some simulation results. Starting from a flat bed, different bed shapes were obtained depending on the droplet size. Three average droplet sizes were used: 2 mm, 3.1 mm, and 6.3 mm. In the 2 mm case, the bed underwent depletion; with the two larger droplet sizes, the bed grew. The bed grew at a higher rate with an average droplet size of 6.3 mm than with a droplet size of 3.1 mm. The beds did not reach a steady-state shape, but continued to be depleted or to grow after the times shown in Figure 14.

It was suggested earlier that the choice of spray model affects the bed shape. The model with both a horizontal and a vertical opening angle (Spray Model 3) was used to calculate the bed shapes shown in Figure 14. For comparison, Figure 15 shows a bed shape simulated with the spray model in which droplets are introduced into the furnace as 11 discrete injections (Spray Model 1) [20]. The uneven distribution of droplets onto the bed results in a bed shape which is less smooth than those in Figure 14.

Although the primary value of the bed shape model is in testing the impact of different parameters on the bed shape behavior, an interesting detail of the simulations discussed here is that they were carried out on a recovery boiler for which images of the actual char bed are available. This made it possible to compare the simulated and the actual bed shapes. The bed shape resulting from an average droplet size of 3.1 mm was found to be in good agreement with the actual bed shape (Figure 16).

Where are we going?
CFD-based models for droplet, gas phase, and char bed burning describe what can be considered the main characteristics of black liquor furnace processes. The modeling approach is based on fundamental theories and concepts. It builds on established expressions for heat and mass transfer, energy and mass balances, and it takes into the consideration differences in the local environment. In addition, the submodels are coupled with each other, thus allowing the different phenomena to happen simultaneously and to interact. Conse-
Figure 15. Calculated bed shape using a spray model in which particles are introduced in 11 discrete directions (Spray Model 1) [20].

Figure 16. Real and simulated bed shapes. Pictures were taken through the same opening in the furnace wall and show the bed on both sides of one mound. The view of the simulated bed is from the same direction, and the portions of the simulated bed corresponding to those seen in the upper figures are indicated with colored boxes [22].

Consequently, CFD models appear to give a reasonable description of combustion in black liquor recovery boilers. At present, their exact prediction capability is uncertain because of the lack of quantified in-furnace data for model validation.

The issue of boundary conditions arises in connection with model validation. The boundary conditions in a recovery furnace simulation include the characteristics of all inflows to the furnace, as well as the characteristics of the furnace walls, e.g., wall temperatures. The simulated combustion is a result of both the boundary conditions and the processes inside the furnace. It has been shown that the models are sensitive to several input boundary conditions, especially the spray characteristics and droplet size distribution. The challenge for accurate simulations is to have representative descriptions of these parameters.

The accuracy of the models is important if the simulations are to be used, for example, in process optimization. However, even without having established the absolute accuracy, response of the models to changes in model parameters can reveal new insights into black liquor combustion, confirm previous understanding, or indicate areas where additional fundamental knowledge is needed. Although the full complexity of the recovery boilers processes is not yet described by
the models, CFD has developed into a research tool, which can be used to study many details in the recovery furnace and to increase our understanding of the overall furnace processes.

The question remains of how CFD-based modeling could develop further. Incorporating more detailed descriptions of the chemistry will extend the models. However, this requires a sound understanding of the chemistry, and there will be a continued need for fundamental experimental data. Areas where our understanding does not yet allow for quantitative modeling include: (i) fume formation and chemistry, (ii) fate and emissions of the gaseous sulfur species (SO$_2$ and H$_2$S), (iii) bed chemistry and the degree of reduction of the smelt. In all these areas the main chemical mechanisms are identified, but determining their quantitative dependence on the various furnace process conditions requires further work.

Perhaps most important is obtaining comprehensive and quantified in-furnace data. Validation would not only establish the accuracy of the current models, but it could make it possible to identify in which respects the models still fail to describe reality. This knowledge could assist in directing further studies and model development.

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References


Introduction

Boiler production is unique manufacturing process. The recovery boiler components made from tubes, pipes and membrane bars are manufactured at workshops, transported to site and erected to finally be operated as one unit. Manufacturing is partly serial production, if the component manufacture is viewed as detailed work. However, boiler manufacturing can also be classified as individual production.

Largest recovery boilers have their own typical features, not only the dimensions and weight but also their own design criteria. So recovery boiler pressure parts can be categorized as a welded product, not as a machine in respect of manufacturing. This approach gives a good possibility to understand the role of tolerances and welding shrinkages related to final product. Basically there are no “moving” components in the pressure parts.

Welded products have typically an image of handwork at least combined together with a big flexible size. Although the aim is towards mechanized or automated production process the site welding is extremely difficult to alter from manual welding to a more productive type.

The size of the modern recovery boiler has increased as shown in the figure 1 and the industrial drivers are mainly economical. This applies as well to boiler manufacture.

The product itself has developed. The demand of higher pressure and temperature leads to use of more alloyed materials and or increased wall thicknesses of the final component. Manufac-

Figure 1. Relative size and capacity increase of recovery boilers.
turing is currently becoming more regulated. This results in detailed instructions, procedures and specifications as well as more educated and trained labor. The requirements for manufacturing and quality have changed during the last decades. The recovery boiler manufacturing technology is today regulated by two major codes/standards: The American Society for Mechanical Engineers (ASME) Section 1 as well as European Standard EN 12952, mainly parts 5 and 6. These standards give very detailed instructions on how to produce boiler components. Also boilers to be built outside USA and Europe are typically based on the previously mentioned standards.

Health, safety and environmental issues in manufacturing have become increasingly important. Not only during the new boiler manufacturing but also during the service of these huge giants must number of requirements be met. The environment at site is clearly different from 60 years ago. This can be realized easily when looking at figures 2 and 3.

**Boiler Size and Manufacturing**

*Dimensions and Weights*

Boiler dimensions have naturally an effect to productivity as well as they from a challenge to manufacturing. Product cost reduction favors big components, dimensions and weights. One of the giant 7000 tds/day recovery boilers currently under construction has the following dimensions; Furnace floor size is 16.5 x 18.0 m and the height of the furnace is about 66 m. The total length of the pressure part tubing is more than 460,000 meters. Huge weight affects also the way this boiler is manufactured. The total weight of the giant recovery boiler pressure parts is about 5200 tons and the total operation hanging load reaches 11000 tons.

**Handling and transportation**

Handling of base material such as very long tubes can be difficult due to the flexibility. The length of the economizer tubes is more than 24 m. Thus even the transportation from the tube mill to the component manufacturing workshop is challenging and therefore tubes with butt welds are accepted today. The economizer tubes are fin welded and the butt welds need to be ground flush.

Special attention is paid to lifting at site. The large recovery boiler components such as superheater and economizer elements are very flexible and the buckling of the components during the lifting is avoided using special lifting frames, several lifting points or at least two cranes. Workshop lifting capacity can be limiting the weight of the com-

![Figure 2. Attitudes on the HSE issues have changed, photo from a boiler erection site, year 1951.](image)

![Figure 3. 7000 tds/day recovery boiler under construction, 2009.](image)
ponents to be handled as one piece. Also road transportation from the workshop to the site has to be well planned. The weight is often causing problems at the site due to need of bigger lifting capacity cranes. These are often much more expensive.

The drums for the large recovery are still manufactured at the workshop. Only a few international manufacturers are able to produce drums with big outer diameter together with heavy wall thickness more than 100 mm. Manufacturing procedures of the drum are more detailed and the allowed manufacturing parameters have a very narrow variation. The transportation and the lifting of the drum require heaviest cranes and vehicles.

**Details of the components**

Welding is always related to joint type, although the trend is to larger component arrays. Recovery boiler manufacturing either small or big has three major joint types: butt welds, nozzle welds and membrane bar to tube fillet welds as shown in the figure 6. The welder must deal with all of these joint types. The major difference is the location of the joint in a large recovery boiler. It is crucial to have welders who are not terrified of heights.

Bending of tubes is similar in small and big recovery boilers. As more steam is produced in big recovery boiler, bigger tube outside diameters must be used. This means heavier wall thicknesses and or stronger materials and therefore the need for heavier bending machines. Heating of the tube or pipe can be used to reduce the needed forces during the bending. Induction heating is typically used for big outer diameter pipes.
Influence of the Product Design

Material Grades
Composite tubes were first time used in the recovery boiler lower furnace in 1971. The outer layer was standard AISI 304 quality. Stainless steel requires cleaner working environment especially during welding. Carbon steel contamination has to be avoided at all cost. During late 80’s special Ni-based alloys such as 825 and 625 composite tube outer layer for lower part of the furnace were introduced. The impurity level at the welding joint area has to be minimized in the workshop or at site. Specially designed electric motors have to be used near the cleaning area in order to avoid explosion if solvents as acetone is used.

One membrane wall for the large recovery boiler can have more than 200 tubes and 400 double fillet welds. The tube tolerances and the welding shrinkages have an effect to the final wall dimensions. Special methods have to be used to achieve the proper size of the wall. In addition different composite tube and membrane grades have different thermal expansion coefficients and shrinkages. The need of a specified grade depends on the temperature, environment, client and manufacturers standards. Almost every boiler furnace has its own material combination. Therefore experience is the key to achieving right dimensions.

Design
There are no extra spaces in a huge recovery boiler. The trend is towards very compact design. Manufacturing and assembly order is well planned as shown in the figure 7.

Fatigue
Long tubes although they are connected to each other are extremely flexible. Mechanical fatigue is one of the essential mechanical design criteria. Risk to fatigue failure can be reduced by smoother weld contours to the base material. The fatigue lifetime can be increased if the angle $\theta$ shown in the figure 6 is larger. This means skilful welders or more costly additional grinding.

Creep
The highest material temperatures are at the creep range in large recovery boilers. Creep loads originate from internal pressure as well as from external mechanical load. Usage of high alloyed creep resistant steels leads to preheating and post weld heat treatments with exactly specified procedures. Welding parameters and welding consumables are selected to meet the creep requirement.

Corrosion
Possible heating surface corrosion has an effect to manufacturing too. The interpass temperature between weld passes is limited for stainless steels, cooling to proper level leads to waiting times. Corrosion can be reduced at superheater area by proper welding consumable selection as well as right heat input during the welding. Carbon steel
contamination of the stainless steels has to be avoided in the final product. It is difficult or at least not productive to protect large areas from carbon steel dust or sparks.

**Workshop and Site Manufacturing**

Bigger components need larger areas to be manufactured in the workshop. Product design requirements are reflected to workshop size and vice versa the workshop space dimensions give guidelines to process and mechanical design. The change of the working area is dramatic as can be seen in figure 8. The workshops today look nearly like offices of older days and enough space is reserved to produce the large components.

**Pre-treatments**

Ferritic tubes are typically grid blasted in order to move the oxide layer as well as the impurities away. This is done to increase the productivity of the welding as well as to raise the quality level for large recovery boiler components. The accuracy requirement is also increased due to length of the components as well as the possible mechanized welding.

**Preheating and post weld heat treatments (PWHT)**

Preheating is carried out before welding and it is local, only located near the weld joints. The difference between small and large recovery of the preheating temperature control comes from the wall thicknesses and material grades used. Post weld heat treatment is more challenging. Furnace sizes are limiting the PWHT to be carried out as one component. Solution for this is carrying out the PWHT in several stages or local. Overlapping of the PWHT area is required if the component is heat treated in stages. Overlapping area means longer exposed heat treatment times for the area. The heat treatment parameters cap where to operate is narrow and it results to more sophisticated control processes related to time temperature sum given to the work piece.
Forming
Forming is mainly bending, also reducing the size of the tubes are needed. Naturally, plate work forming is concentrating to the drum; heads and shell. Bigger components together with high strength materials need stronger equipment to carry out the forming and even more the hot forming. Temperature control during the hot forming of the thicker material needs sophisticated temperature measurements as well as skill. One of the key factors in bending is ratio of bending radius (R) divided by outer diameter (D). Smaller R/D is required to pack the superheater into smaller space. This means either hot bending or cold bending with more detailed and specified bending parameters. More knowledge related to bending parameters such as compression forces during bending is often required to perform superheater bending especially using composite tubes and solid stainless tubes.

Welding
The amount of welding is dramatically increased in the giant recovery boiler manufacturing. Therefore, the trend is towards mechanization and automated production, in order to keep the production cost low. Economizers can have tube to fin fillet about 350 km and the length of the composite fillet weld in the furnace can be roughly about 100 km.

The challenges to mechanize or automate the manufacturing process are the dimensions of the components, tolerances of the base tube material and welding shrinkages. The weld joints cannot be located before and during the manufacturing process with enough accuracy in order to place the welding torch exactly to the right position. Site welding mechanization is even more challenging not only because work is done at elevated level. Huge amount of scaffolding is needed and the prevention from the effects of wind and rain is required. The roots of the welds are welded with TIG welding process requiring shielding gas. Root gas is also needed for highly alloyed materials and good shielding for root area is difficult to achieve due to long distances from open place and the root area of the welding joint.

Labour
Welders have been qualified already for 40 years in boiler manufacturing. It is important for a welders manufacturing large size recovery boiler to understand the procedures. The information of manufacturing methods, parameters and rules are issued in these documents.

All these modern giant recovery boilers are located outside of Scandinavia. Naturally, skilled workers can be found in Asia especially in South America. Transferring the manufacturing requirements needs also very experienced manufacturing supervisors. It is not enough to transfer the technical and quality information but also to understand the local culture and way of working.

Quality
The basic quality requirements come from the used code and standards. In addition, manufactures have their own rules based on their design and customers have mill standards. In order to control that the work is carried out according to contract and rules authorized inspectors are used, third party inspectors from client side and naturally manufactures own personnel are involved.

To be able to manufacture large recovery boiler manufacturer shall have a quality assurance sys-
tem, which will be continuously revised and checked in the audits. Same inspection methods are used for inspection of small and large recovery boiler; only increased amount of isotope is used instead of x-ray inspection. Traceability of the welds is very typical for the joints in recovery boilers: what manufacturing procedures have been used, records how the manufacturing have been carried out and who has done the work not neglecting the material traceability.

Non-conformance reports are used as a tool to record components or their parts if they do not fulfill all the requirements stated before commencing of the manufacturing.

**Conclusion**

The main difference between large recovery boiler manufacturing and small is basically the dimension and the weight of the components. This means more challenges during the component transportation from the workshop to the site. Lifting the components must be planned with more detail.

The product design, bigger amount of steam flow and higher steam parameters have lead to thicker materials as well as using more alloyed materials. Manufacturing has to take into account flexibility of the mechanical design and finalize the welds with smooth contours to avoid fatigue. Large recovery boiler welder at site will be one of the last handwork professions although productivity and therefore mechanization and automated production is the target.

Manufacturing is not the limiting factor producing even bigger recovery boilers but then the productivity may decrease. The quality of manufacturing has been increased resulting on operation that is more reliable. Big recovery boiler has been a forerunner showing the quality requirements and if small size recovery boiler is manufactured in the future it will adopt the same standards and requirements as big recovery boilers today even if that detail of attention is not needed.
The challenge today’s recovery boiler owners face is how to ensure high boiler availability and energy efficiency and low emissions without jeopardizing the safety issues. The recovery boilers in Sweden are today fired with increasingly higher dry solids black liquor containing relatively high amounts of non-process elements.

In 2006, the Swedish-Norwegian Recovery Boiler Committee (SNRBC) initiated a three-year process study regarding the state of the art recovery boiler technology called “Förutsättningar för framtidens sodapanna” (the Opportunities of future recovery boilers). The study aimed to find those factors that will be crucial for the future recovery boiler development in respect to safety, low emissions and energy efficiency.

Background

The recovery boiler technology has developed considerably during the last 15 years in Sweden. The liquor dryness has increased from 70% DS content to 80% DS content or more. The boilers are bigger and have larger cross sectional area than before. New air systems have been implemented which enable more flexibility in liquor combustion. On top of this, more process streams are led to the evaporation plant and the recovery boiler than before, increasing the NPE load. The emission regulations have been tightened and especially the NO_x – regulations limit the degrees of freedom in liquor combustion.

The recovery boiler park of the SNRBC was some 30 years old in 2005. Several smaller boilers were then – and are even more so today – close to the end of their technical service life. There are also several mills with more than one recovery boiler, while the international trend is one mill – one recovery boiler.

In the period 2005-2008, three new high pressure recovery boilers were taken into operation (Stora Enso Skoghall 107 bar/500°C, SCA Östrand 106 bar/515°C and SCA Obbola 110 bar/505°C). In Skoghall’s case, a new evaporation plant was also taken into operation, enabling high liquor dryness, 80% DS content or more. These three boilers are expected to be in operation until the year 2040 or longer.

In the future even higher steam data and/or liquor dryness can be predicted. A Japanese recovery boiler is reported to operate at 133 bar/515°C steam data. The UPM Wisaforest and Metsä-Botnia Kemi mills are reported to burn 85% DS liquor. The evaporation plant manufacturers have demonstrated that evaporation to 90% liquor DS is feasible.

The starting point for the process that led to this study was the 40th anniversary of the SNRBC in 2005. A workshop was held at the anniversary to plan the activities for the committee for the next three years. The members expressed an almost unanimous desire for a new process study on recovery boiler combustion and operation.

These targets are not expected to materialise without effort. As the members stated at the workshop, there are difficulties in recovery boiler operation today. Furthermore, the operation of modern state-of-the-art boilers can be more difficult. The operation of future, more advanced recovery boilers, can be even more difficult to handle.

Already in 2005 an inquiry was sent to Stora Enso Skoghall mill regarding the possibility to conduct mill trials at the then brand new high pressure recovery boiler. The inquiry was well received and Skoghall agreed to participate in the project, if external funding could be secured.
The Board of the SNRBC decided in 2006 to initiate a three-year process study on state-of-the-art recovery boilers based on the opinion of the members from the workshop in 2005. The study was called "Förutsättningar för framtidens soda-panna" (The opportunities of future recovery boilers) or just "3FS" in Swedish.

This study tried to answer to the questions that have been raised operating recovery boilers with increasingly higher dry solids black liquor and steam data, higher NPE content, new air systems and bigger recovery boilers. The members of SNRBC can benefit from these answers, especially if they plan to apply for two-year operation between internal and external inspection. Another motive for the study was to collect and analyse the process information from one modern recovery boiler and make these results available to all members.

Two similar studies were conducted by the SNRBC earlier. In 1987-1988 a study called "Förbränningsteknisk undersökning i sodahus" (A combustion technology investigation of a recovery boiler) was undertaken. In 1989-1991 another study called "Förbränning och korrosion i sodapannor" (Combustion and corrosion in recovery boilers) was completed. These studies were funded by the SNRBC with the aide of public and private research foundations.

The Project
A separate project organisation was set up by the SNRBC to manage the project. A project team was formed, headed by Per Utterström, Korsnäs Gävle. The team included members from ÅF and Stora Enso. Two reference groups were connected to the project team, with representatives from SCA, Metso Power, M-Real and Södra Cell.

The total cost for the project was calculated to be 2.3 MSEK in 2006. The SNRBC allocated 1 MSEK for the three year period. Additional funding was received from Åforsk, the ÅF Research Foundation, and Värme forsk, the Thermal Engineering Research Institute, 650 000 SEK each. See Table 1 below for details.

The members of the SNRBC have also contributed with manpower in-kind to the study. Additionally, the mill personnel at Stora Enso Skoghall mill helped the project with manpower and analyses worth several 100 000 SEK in-kind.

The project was officially initiated in April 2006. During 2006 and most of 2007, the mill trials were planned and preparations made. The mill trials were delayed a few months and were completed November 26th to December 1st, 2007. Results and analyses were completed during 2008. The final report was issued to Åforsk and Värme forsk in the second week of 2009.

The project was reported to the Board and members of the SNRBC during the course of the work. A report was issued to the two external financers Värme forsk and Åforsk. The project was also reported at the Swedish and Finnish Recovery Boiler conferences and the AF&PA's Recovery Boiler conference.


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Subprojects
The SNRBC project team decided to split the project into four subprojects.

Subproject Process technology
In this subproject, all process measurements and sampling was done in the Skoghall recovery boiler. Originally, the subproject was planned to be executed in September 2007. This was pushed forward to November due to a digester plant capacity increase. This allowed for a higher recovery load.

First a so called reference run was made. During this 24 hrs test run, the boiler was run at maximum available liquor load at normal liquor dryness, 80% DS. After this test run, the liquor dryness was planned to be raised to 83% DS or more. The evaporation plant was pushed to the limit, during which the liquor dryness was targeted to be 83% DS or more. This elevated liquor dryness was kept for two consecutive days, during which the actual project measurements and sampling were made.

The following samples were taken and measurements done:

- Liquor samples for dry solids and composition analysis.
- Ash samples from the boiler bank and economiser areas and from the electrostatic precipitator for composition analysis.
- Some 300 boiler instruments were tagged (one minute averages) for a total of four days.
- Dissolver off-gases and dissolver off-gas condensates for various analyses.
- HVLC gases and condensates for various analyses.
- Smelt from inside the smelt bed with a special probe designed by ÅF. A number of analyses were carried out.

Subproject Material science
This subproject handled all the material science issues. Åbo Akademi University was subcontracted to measure the fouling build-up and composition in the superheater area of the Skoghall boiler. These measurements were made simultaneously with the process technology subproject.

Subproject NOX
The purpose for this subproject was to investigate the nitrogen content in the process flows going in and out from the recovery boiler. Additionally, an important part was to investigate the combustion conditions at the tertiary air level in the boiler, where the unburned gases from the lower part of the boiler are oxidised. The reason for this was to find if the combustion of the dissolver off-gases in this air level were beneficial from a NOx emission point of view.

Åbo Akademi University was subcontracted to take smelt samples from the smelt spouts in Skoghall and analyse these and the smelt samples taken from inside the smelt bed for nitrogen (cyanate) compounds. The Skoghall mill was conducting a millwide nitrogen assessment during the period that the 3FS project was executed. Some information from that study was utilized in this study.

Subproject Energy efficiency
The idea with this subproject was to make a technical potential study of how to improve the energy efficiency of a state-of-the-art recovery boiler similar to Skoghall’s boiler by using advanced simulation tools. A model of Skoghall’s recovery boiler was set up and the boiler performance was calculated for 80%, 83% and 90% liquor dryness. After this, the boiler was “fitted” with intermediate steam superheating, feed water preheating and a flue gas cooler. The impact of these technologies was simulated one by one and in combination to give an insight into how much the energy efficiency could be improved.

Measurements in Skoghall
The measurement campaign was successfully executed from November 26th to December 1st, 2007. The sampling and measurement points are shown in Figure 1.

During Monday the 26th the last preparations were made. One GC was installed in a sampling booth located in the Skoghall boiler stack to measure the nitrogen compounds. Another GC was prepared in Skoghall’s lab to analyse the sulphur compounds. Sampling bottles and cans were distributed. Skoghall’s dayshift and lab personnel were given a briefing on the final measurement plan. Åbo Akademi University conducted a functionality test of the fouling probes that afternoon.

The reference run at the planned 80% liquor dryness and 1900 tDS/24 h liquor load was executed on Tuesday 27th. All samples were successfully extracted, except the gas samples from the lower furnace. In this location the sampling tubes melted. Smelt samples were also successfully extracted.
Figure 1, Sampling and measurement points in Skoghall. Sampling points for medium heavy liquor, HVLC gases and HVLC condensate not shown.

from inside the smelt bed. About a dozen samples were taken. A few images of the measurement and sampling activities are shown in Figure 2.

During Wednesday afternoon, the evaporation plant was tuned up to start increasing the liquor dryness. The target dryness was set to 83.5% DS. Raising the liquor dry solids content was surprisingly easy.

The long anticipated 3FS-test run was executed from Thursday November 29th to Saturday morning December 1st. Skoghall’s recovery boiler was run at around 83.5% DS and 1900 tDS/24h. Like two days earlier, all planned samples were collected. After the measurement campaign was completed, liquor, smelt, condensate and boiler ash were sent to the Swedish Technical Research Institute for analysis. Åbo Akademi University analysed the cyanate content of the smelt samples and the chemical composition of the fouling collected in the superheater area.

In 2008 it became known that there had been a leak of medium pressure steam in the primary air preheater. It is not known how this leak affected the measurements.

Results and discussion

General recovery boiler performance

The results from the liquor analyses are shown in Figure 3 below. Note that it is very difficult to determine the dry solids content for black liquor
Figure 2, Measurement and sampling activities in Skoghall. Clockwise from top left: nitrogen compound analyser in flue gas stack – sampling point for dissolver vent gas condensate – fouling probe in place – temperature measurement of smelt bed through primary air port with radiation pyrometer.

Reference
run
High solids run

Figure 3, Dry solids content of as-fired liquor during the reference and 3FS firing. The lower curve indicates the dry solids content of medium heavy liquor prior to the ash mixing and the superconcentrator.

with extremely high dryness.

Table 2 below shows the composition of the as-fired liquor during the three test days.

It is apparent that the target set regarding liquor dryness was met. The mill instrumentation registered 83.5% to almost 84% liquor dry solids content during the high solids firing. On average, the dry solids content was raised from 82% DS to 85% DS. The composition remained very stable
during the entire test period.

A large number of boiler ash samples were collected. The results are compiled below, Table 3.

The following conclusions can be made
1. The chloride level is relatively low. There is very little difference between the normal and the high dry solids liquor. The same is true for potassium.
2. The carbonate level is somewhat higher during the high dryness test firing than during the reference run. This is as expected and points to that the furnace has been hotter during the high dryness test.

The trends for boiler feed water flow, steam flow and as-fired liquor flow coincide during the refer-

Table 2, The composition of as-fired black liquor during the entire period (collected sample during one day, mass-% of dry sample).

<table>
<thead>
<tr>
<th></th>
<th>Reference run</th>
<th>High solids day 1</th>
<th>High solids day 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>%</td>
<td>32</td>
<td>31,7</td>
</tr>
<tr>
<td>H</td>
<td>%</td>
<td>3,1</td>
<td>3,3</td>
</tr>
<tr>
<td>N</td>
<td>%</td>
<td>0,07</td>
<td>0,06</td>
</tr>
<tr>
<td>S</td>
<td>%</td>
<td>6,4</td>
<td>5,9</td>
</tr>
<tr>
<td>Cl</td>
<td>%</td>
<td>0,23</td>
<td>0,21</td>
</tr>
<tr>
<td>Na</td>
<td>%</td>
<td>20,1</td>
<td>20,6</td>
</tr>
<tr>
<td>K</td>
<td>%</td>
<td>1,54</td>
<td>1,56</td>
</tr>
<tr>
<td>Dryness (%)</td>
<td></td>
<td>82,4</td>
<td>85,5</td>
</tr>
<tr>
<td>HHV&lt;sub&gt;DS&lt;/sub&gt;</td>
<td>MJ/kg</td>
<td>12,68</td>
<td>12,75</td>
</tr>
</tbody>
</table>

Table 3, The composition of the boiler ash, mass-% average.

<table>
<thead>
<tr>
<th></th>
<th>Reference run</th>
<th>High solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiler bank</td>
<td>Na</td>
<td>34,6</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>3,2</td>
</tr>
<tr>
<td></td>
<td>SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>50,4</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>0,7</td>
</tr>
<tr>
<td></td>
<td>CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>14,2</td>
</tr>
<tr>
<td>Eco 1</td>
<td>Na</td>
<td>33,2</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>3,6</td>
</tr>
<tr>
<td></td>
<td>SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>53,1</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>1,0</td>
</tr>
<tr>
<td></td>
<td>CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>10,9</td>
</tr>
<tr>
<td>Eco 2</td>
<td>Na</td>
<td>34,0</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>3,6</td>
</tr>
<tr>
<td></td>
<td>SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>53,3</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>1,0</td>
</tr>
<tr>
<td></td>
<td>CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>10,5</td>
</tr>
<tr>
<td>Elec. precipitator</td>
<td>Na</td>
<td>32,7</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>3,7</td>
</tr>
<tr>
<td></td>
<td>SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>53,4</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>1,1</td>
</tr>
<tr>
<td></td>
<td>CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>10,4</td>
</tr>
</tbody>
</table>

Based on results from the Technical Research Institute of Sweden
ence run and the high solids test firing. This indicates that the boiler has been running evenly with no unexpected swings. The trend is illustrated for the second day of high solids firing in Figure 4.

The average temperatures in the upper part of the furnace and the boiler are shown in Figure 5. The data is compiled from the trend data downloaded from the DCS. The “furnace” temperature is in this case the temperature at the tertiary air port level. What can be seen is that the average temperatures between the reference run and the high solids firing test does not exhibit any major difference in the chosen locations. Note that the average temperatures during the high solids test are equal or even lower than during the reference run.

Figure 4. Second day of high dry solids firing. Flow of feedwater, steam and as-fired liquor.

Figure 5. Flue gas average temperatures in various parts of the recovery boiler.
Figure 6. Measurement points for the deposit measurement probes.

Figure 7. Deposit growth rate (mm/h) in sampling points MP1 and MP2 (Reference run dark grey, high solids firing light grey).
**Fouling, carry-over and ISP’s**

Åbo Akademi University measured the fouling with a special fouling probe. The probe was inserted in the superheater area of the Skoghall recovery boiler, Figure 6.

The deposit growth rate was higher on the wind side of the probe. The following growth rate was observed for sampling points MP1 and MP2 just above the bull nose, Figure 7.

The deposit growth rate for sampling points MP3 through MP6 was below 1 mm/h. The principal composition of the deposits at each location is as follows:

- **MP1:** carry over and ISP
- **MP2:** almost exclusively ISP
- **MP3-MP5:** ISP and fume
- **MP6:** fume

The amount of sodium and sulphate in the deposits in all sampling points are shown in Figure 8 below.

The deposit measurements can be summarized as follows:

1. The increased dry solids content does not affect the amount of deposits in any major way.
2. The deposit growth rate in MP2 through MP6 is correlated to the temperature of the sampling point. The deposits become sticky or have started sintering at 700-750°C.
3. The sulphate formation in the carry over takes place earlier in the superheater area at high solids firing.

An earlier study of deposits in Swedish recovery boilers was made by Åbo Akademi University, Figure 9. The study was financed by Värme forsk, [6]. Deposit measurements in a total of six recovery boilers were made. Two boilers were measured twice, hence eight results (A-H) in the figure. These six boilers represent normal Swedish technical status. None is even close to the liquor dryness and steam data of the Skoghall recovery boiler.

Skoghall’s three collected results (reference, high solids firing day 1 and 2) are placed to the right in Figure 9.

The conclusions with respect to Skoghall are as follows:

1. In Skoghall’s deposits there is more Na but the K-level is at the same level as in the deposits of the other six boilers.
2. The chloride level is approximately the same as the Cl-level in the other six boilers during the reference run and the first day of high solids firing. The elevated chloride level on the second day of high solids firing remains a mystery. The amount of chloride in the as-fired liquor does not change, see Table 2. It is possible that this is only a coincidence. The amount of chloride in the boiler ash changes very little between the reference run and the high solids test run. Skoghall’s sulphidity is 32-33% which should not affect the chloride level.
3. The deposits contain more carbonate during the high solids firing. This points to that the furnace temperature was higher during the test run. This was expected.

![Sodium and Sulphate Content](image)

*Figure 8, Sodium and sulphate content of the deposits in all sampling points (mass-%).*
Figure 9. Deposit measurements in six Swedish recovery boilers and the Skoghall recovery boiler (mass-%).

No accelerated corrosion tendencies were found in the superheater area during the annual outage and inspection in the fall of 2008.

Other factors affecting the deposit composition is the pulp mill sulphidity, pulp wood and processes used (soap firing, mixing residual acid into the firing liquor, chloride enrichment). The overall conclusion is that Skoghall’s deposits are not exceptional in any way, apart from the higher carbonate content, during normal and high solids firing.

Smelt composition

Half of the smelt samples from the smelt bed were sent to the Technical Research Institute of Sweden for analysis. The other half was sent to Åbo Akademi University for cyanate and carbon analyses.

The results are shown in Figure 10 below.

The levels of sodium and carbonate show some variation. On the contrary, the levels of carbon and potassium are relatively stable. The chloride level is very low.

What makes Figure 10 extra interesting are the two extra bars to the right in the figure. These represent the min and max carbon levels in the smelt samples taken from Södra Cell Mörrum’s state-of-the-art recovery boiler in 1990. With the firing techniques and air systems of that day, a reduction degree of 90% could be reached. The reduction degree in Skoghall was 95%, despite that the carbon level in the smelt was at the lower limit of what was found in Mörrum. The reason for this improved reduction degree is subject to discussion. One hypothesis put forward is that a part of the reduction reaction can take place in suspension, i.e. after the liquor droplet has dried and devolatilized.

The lower carbon content in Skoghall’s smelt bed became evident during the sampling. The smelt burned with an open flame in when it was taken out of the smelt probe in Mörrum. It is thereby likely that the actual carbon content may have been higher than what is shown in Figure 10. When the smelt sampling probe was opened in Skoghall, the smelt glowed but did not burn.

Another observation made in Skoghall was the impact of increased boiler size. Twenty years ago, most boilers had sloping floors and a smaller cross-sectional area than today. Smelt beds could be quite high. This means that in Mörrum smelt could be taken to a depth of some 50 cm into the bed. During the bed sampling in Skoghall, only smelt from the active surface could be taken (0-20 cm). This is due to the fact that Skoghall’s recovery boiler has a cross-section of some 10 x 10 m and the decanting floor gives a low smelt bed.

NO$_x$ emissions

During the reference run and the high solids test, a number of nitrogen compounds at several loca-
tions were monitored. The focus was on the flue gas and the dissolving tank vent gases fired in the tertiary air level. The levels measured in the flue gas are shown in Table 4.

The difference between the NO- and the NO2-levels are small for the reference run and the high solids test. The levels of N2O and NH3 are at the detection limit.

These results differ from the earlier 1987 results. A similar high solids test firing was then undertaken in the then state-of-the-art recovery boiler nr 5 in Korsnäs. The liquor dryness was increased from 65% DS to about 76-77% DS for one day. During this test firing, the NO -level increased with some 60% in the flue gas. In absolute numbers from 95 ppm dry gas to 155 ppm dry gas.

Nothing like this could be detected in Skoghall. It must be noted though, that a liquor dry solids increase from 65% DS to 77% DS is much more dramatic than an increase from 82% DS to 85% DS. It seems unlikely that this NOX-level increase in Korsnäs would be due to thermal NOX formation, since the furnace temperatures measured then were well below 1400°C.

**Combustion of dissolving tank vent gases in the tertiary air level**

Skoghall fires the dissolving tank vent gases in the tertiary air level. The amount of gaseous ammonia in these vent gases was measured to be 273-331 mg/m3n dry gas during the reference run. During the high solids test firing, the ammonia increased to 299-393 mg/m3n dry gas. This corresponds to an increase of some 20-60 mg/m3n dry gas as a result of the higher liquor dry solids content. There are few comparable measurements. Tarpey et al [7] reported a level of 250 mg/m3n dry gas in a Canadian mill in 1996.

The dissolving tank vent gases are fed into the tertiary air level from one side only. The average temperature at this level was already shown in Figure 5. The temperature was also measured by hand held radiation pyrometers a few meters below the intake of the vent gases, through the liquor gun openings. In this location, the average temperature was 1079°C during the reference run and 1091°C during the high solids test firing. It is generally known that ammonia reduces nitrogen oxides to nitrogen in the temperature window of 850-1000°C. If the NH3 is added at higher temperatures, it forms NO instead [8].

**Table 4, Nitrogen compounds in the flue gas from Skoghall’s recovery boiler during the entire test firing period (average amount in ppm dry gas).**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Unit</th>
<th>Reference run</th>
<th>High solids day 1</th>
<th>High solids day 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>ppm dg</td>
<td>100</td>
<td>104</td>
<td>99</td>
</tr>
<tr>
<td>NO2</td>
<td>ppm dg</td>
<td>1,4</td>
<td>2,4</td>
<td>3,3</td>
</tr>
<tr>
<td>N2O</td>
<td>ppm dg</td>
<td>&lt;0,1</td>
<td>&lt;0,1</td>
<td>&lt;0,1</td>
</tr>
<tr>
<td>NH3</td>
<td>ppm dg</td>
<td>0,9</td>
<td>0,3</td>
<td>0,3</td>
</tr>
</tbody>
</table>
This phenomenon was observed during the high solids test period. The dissolver off-gases were bypassed to the stack four times and were then substituted with combustion air. During these periods (up to two hours at a time) a decrease in the NOX-level in the boiler flue gas could be observed. The NOX-levels were also fluctuating less during these periods.

Figure 11. below shows the NO- and O2-level during the reference run. The NO-level fluctuates, while the O2-level is fairly constant at 3%.

Note the effect on the NO-level when the dissolver vent gases are bypassed, Figure 12 and Figure 13. Interestingly, the amplitude in the NO-level fluctuations is also less during these periods.

Figure 11. NO- and O2-content of the flue gas during the reference run. Dissolver off-gases are mixed and burned in the tertiary air level. Note the amplitude of the fluctuations in the NO-content.

Figure 12. NO- and O2-content of the flue gas during the first day of the high dry solids run. Dissolver off-gases are vented to the atmosphere between 3-4 pm and 7-9 pm; otherwise these are mixed and burnt in the tertiary air level.

The conclusion is that the \( \text{NH}_3 \) content in the dissolver vent gases is increasing the NO\(_X\)-emission of the boiler (!). Although the dissolver vent gases were not bypassed during the reference run there is no doubt that this phenomenon would also be found during normal black liquor solids firing.

**Smelt sampling and smelt nitrogen content**

Åbo Akademi took smelt samples from four smelt spouts during the reference run and the high solids firing. The results are shown in Figure 14. The amount of nitrogen as cyanate (OCN\(^{-}\)) in the smelt samples from the spouts 1, 3, 4 and 6 are shown.

The cyanate content in the middle spouts (3, 4) was on average 0.032% during the reference run. The content in the outer spouts (1, 6) was on average 0.014%. As for the first day of the high solids firing, the amount in the middle spouts increased to 0.036% on average. The outer spouts contained on average 0.017% cyanate.
ÅF took temperature measurements of the smelt in the spouts during the entire test week. The average smelt temperature was 905°C during the reference run and 884°C during the high solids firing. These measurements were difficult to perform and there may be several sources of error in the individual measurements. However, the conclusion is that the smelt temperature was quite normal.

The following conclusions can be drawn regarding the smelt cyanate content:

1. The smelt cyanate content is lower in the outer spouts (1, 6) than in the middle ones (3, 4).
2. The cyanate level is about 10% higher during the high solids firing. However, there was no clear difference between the two measurement series.

Åbo Akademi University also received samples of the bed smelt taken from inside the boiler. These were analysed for cyanate (and carbon), Table 5.

Note that the amount of cyanate in the bed smelt exhibits a wide variation and that the absolute level is close to the amounts found in the outer smelt spouts (1, 6).

A nitrogen balance for the recovery boiler and dissolver vent gas system has been set up based on the measured amounts of nitrogen compounds, known process flows to the recovery boiler and calculated smelt flows in the spouts. The balance for the reference run is shown in Figure 15. The balance for the high solids firing test is shown in Figure 16 (average for both days).

It is obvious that the balance does not add up. According to [9], approximately one third of the nitrogen in the black liquor should be found in the smelt going out from the boiler. The balance around the boiler only adds up if the N₂-amount in the flue gas is calculated to 35-38 kg/h. The distribution of gaseous nitrogen compounds is not according to theory with this calculated amount of N₂. The amount and share of NOₓ is according to theory, but the N₂ flow is twice the expected amount.

The amounts of cyanate in the smelt are low according to Åbo Akademi University. The carbon content is also low. Since char = carbon plays a role in the cyanate transport to the smelt bed, the question can be raised if the low cyanate and low carbon content in the smelt are connected somehow.

Also note the total nitrogen content of the dissolver vent gases. These contribute with approximately 10% of the amount of nitrogen influx with the black liquor to the total nitrogen influx to the boiler.

Stora Enso Skoghall made a nitrogen balance over the entire Skoghall mill in June 2007. The following measurements were made, Table 6.

In this study, the nitrogen content in the medium heavy liquor was measured. Thereby a straight comparison with the amounts found in Figure 15 and Figure 16 is not applicable. In this study the measured NOₓ emission is lower than for the ref-

---

**Table 5. Amount of cyanate in samples taken from the smelt bed in Skoghall (mass-% of total smelt).**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cyanate</th>
<th>Total carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>ÅF-BäSm-01</td>
<td>0.006 %</td>
<td>2.49 %</td>
</tr>
<tr>
<td>ÅF-BäSm-02</td>
<td>0.007 %</td>
<td>4.80 %</td>
</tr>
<tr>
<td>ÅF-BäSm-03</td>
<td>0.006 %</td>
<td>4.50 %</td>
</tr>
<tr>
<td>ÅF-BäSm-04</td>
<td>0.021 %</td>
<td>5.47 %</td>
</tr>
<tr>
<td>ÅF-BäSm-05</td>
<td>0.025 %</td>
<td>4.97 %</td>
</tr>
<tr>
<td>ÅF-BäSm-06</td>
<td>0.004 %</td>
<td>5.11 %</td>
</tr>
<tr>
<td>ÅF-BäSm-07</td>
<td>0.008 %</td>
<td>5.10 %</td>
</tr>
<tr>
<td>ÅF-BäSm-08</td>
<td>-</td>
<td>5.05 %</td>
</tr>
<tr>
<td>ÅF-BäSm-09</td>
<td>0.037 %</td>
<td>5.28 %</td>
</tr>
</tbody>
</table>
Figure 15, Nitrogen balance for the recovery boiler and dissolver vent gas system during the reference run.

Figure 16, Nitrogen balance for the recovery boiler and dissolver vent gas system during the high dry solids run.
erence run and the high solids firing. The measured amounts of N for the green liquor, white liquor and the scrubber discharge are at the detection limits; thereby the results can be uncertain.

The scrubber discharge is led to the green liquor together with the dissolving vent gas scrubber condensate. Even if all this nitrogen would end up in the vent gases, it is unlikely that this extra nitrogen could explain the unbalance between the nitrogen coming in to the dissolver with the smelt and the nitrogen leaving the vent gas from the dissolver vent gas system.

**Energy efficiency**

A state-of-the-art recovery boiler similar to Skoghall’s recovery boiler was simulated with boiler feed water steam preheater, intermediate steam superheater and a flue gas cooler. No energy balance for an entire pulp mill was set up, only the impact of the recovery boiler changes to the bark boiler and the steam turbine were considered. All mills have different energy solutions. This was a pure technical potential study, no economical considerations were included. The simulation results are shown in Figure 17.

Abbreviations and x-axis legend explanation:
“Basfall”: base case
“MÖH”: intermediate steam superheating
Example:
“80% 190°C 4 12 28 bar MÖH” = 80% dry solids; air preheating to 190°C; 4, 12 and 28 bar steam used for BFW preheating; intermediate superheating.

Table 6, Nitrogen balance for the recovery boiler and recausticizing in Skoghall.

<table>
<thead>
<tr>
<th>Location</th>
<th>Amount (g/l)</th>
<th>Flow (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N in medium heavy liquor, before the mix tank</td>
<td>0.052 mass-%</td>
<td>31.8</td>
</tr>
<tr>
<td>N as NOx from the recovery boiler</td>
<td>11.4</td>
<td></td>
</tr>
<tr>
<td>N in green liquor</td>
<td>&lt; 0.02</td>
<td>&lt; 3.3</td>
</tr>
<tr>
<td>N in white liquor</td>
<td>&lt; 0.02</td>
<td>&lt; 2.5</td>
</tr>
<tr>
<td>N in scrubber discharge (recausticizing)</td>
<td>&lt; 0.02</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Figure 17, Simulation results. The base case is Skoghall’s recovery boiler at design load. Incremental increase compared to base case (%).
The following conclusions can be drawn:

- There is a technical potential to increase the power output of a recovery boiler – bark boiler combination by use of boiler feed water steam preheating and intermediate steam superheating.
- The potential is considered to be good already with boiler feed water steam preheating by using normal process steam up to steam used for soot blowing.
- Increasing the liquor dry solids contributes less to increased power output than boiler feed water steam preheating and intermediate steam superheating.
- The possibility to fully estimate the technical potential is limited by the fact that when boiler feed water steam preheating and intermediate steam superheating are used, the other heating surfaces should be adapted accordingly.
- When using boiler feed water steam preheating and intermediate steam superheating, the recovery boiler layout should be modified as follows:
  - Larger superheaters
  - Smaller boiler bank
  - A flue gas cooler must be used
  - The recovery boiler water circulation system must be enlarged
- The investment cost is assumed to increase for the recovery boiler.
- The optimal solution for each case can only be found by making an economical optimization based on the local conditions.

Conclusions
Based on the high solids test run, it is striking that the difference between firing 82% DS liquor and 85% DS liquor is not greater. The mill personnel experienced the high solids test firing as a smooth ride with the boiler. The entire project must be considered a success.

The major conclusions are:

- Skoghall’s recovery boiler exhibits good run ability and low emissions at normal and high dry solids firing.
- There are indicators that the furnace and the smelt bed were hotter during the high solids test firing than during the reference run.
- The ammonia content of the dissolver vent gases is substantial and affects the total emission of NOX from the boiler, in this case by increasing it. If dissolver vent gases are to be fired in a recovery boiler, these should be added to a temperature zone below 1000°C. By doing this, the NH₃-content will decrease the NOX emission.
- The amount of nitrogen in the smelt is lower than expected.
- The amount of carbon in the smelt bed is lower than previous measurements, but the reduction degree is still high.
- The deposits in the superheater area exhibit no extraordinary composition and there is little risk of accelerated corrosion tendencies during present firing conditions.
- The energy efficiency calculations show that, under certain conditions, the power output can be increased significantly with boiler feed water steam preheating, flue gas cooling and intermediate steam superheating.

Future work
This study has come up with some interesting results that merit further investigation:

- Continued measurements of the ammonia content in recovery boiler dissolver vent gases in Sweden.
- In depth studies of the NOX emissions in those recovery boilers that fire dissolver vent gases in the boiler (Billerud Gruvön, Södra Cell Värö, Stora Enso Skoghall, SCA Östrand, SCA Obbola).
- Further sampling of the smelt bed in recovery boilers firing high dryness black liquor to increase the knowledge of the bed chemistry and dynamics.
- In depth studies on the reduction reaction in the lower furnace and possible reaction steps taking place in suspension.

Acknowledgements
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Without the support and effort of the members of the SNRBC – and especially the personnel of Stora Enso Skoghall mill – this study would not have been possible. Their support is gratefully acknowledged.
References
5. Bruno, F; Thermo chemical aspects on chloride corrosion in kraft recovery boilers. NACE Corrosion 2001 Conference, Houston Texas USA 2001
BLACK LIQUOR PARTICLE AND DROPLET REACTIONS: EXPERIMENTAL AND MODEL RESULTS

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PROVO, UT 84602

Introduction

During papermaking, a mixture of sodium hydroxide (NaOH), sodium carbonate (Na$_2$CO$_3$) and sodium sulfide (Na$_2$S) at elevated temperatures dissolves lignin in wood chips, releasing insoluble cellulose fibers in a process called digestion. The lignin acts as a binder in the wood to hold the fibers together and constitutes about 30% of the wood mass [1]. Lignin has several detrimental impacts on paper; so digestion and washing/separation steps remove lignin from cellulose fibers in papers with quality above newsprint. The digester effluent stream containing mostly dissolved lignin-based organic materials and spent alkali salts is called black liquor and is referred to as weak black liquor in the state that it leaves the digester. Evaporators concentrate the weak black liquor to strong liquor with 65-85% solids content to promote its combustion [2]. The so-called solids refer to the non-water portion of the liquor – they form solids after complete drying of the liquor, but essentially all of these so-called solids are either dissolved or in suspension in the liquor and in these senses are more liquid than solid in practice. In the concentrated or strong black liquor, the solids mainly comprise sodium salts and lignin-based organics in solution with some precipitates and impurities as suspended solids and small amounts of potassium, chlorine, silica, and other impurities. These last impurities come from inorganic components and contaminants in the wood and collectively represent the non-process elements. Recent trends increase the solids content of strong black liquor to 80-85% to decrease the possibility of water-smelt explosions and increase the throughput of the recovery boiler [3].

A profitable and environmentally acceptable paper mill recycles the valuable and otherwise environmentally aggressive inorganic salts. The lower section of the recovery boiler and the char bed operate at a locally reducing stoichiometry in some regions, reducing oxidized inorganic components of black liquor to more active solubilizing agents that eventually return to the digester, and at locally oxidizing stoichiometries in other regions, oxidizing organics to produce heat and light-gas products. The primary role of the recovery boiler involves separating the salts from the organics, recovering the inorganics for recycle and heat from the organics – it recovers chemicals and heat. Black liquor is the second largest renewable energy source in North America and Europe, following hydropower and – depending on how one classifies fuels – about the fifth largest fuel of all types, distantly following coal, petroleum, natural gas, and nuclear fuel [4].

Black liquor impinges on a splash plate as it enters the boiler, forming droplets in the range of 0.5 to 5 mm in diameter. As these droplets pass through the boiler, they undergo different stages of combustion. The stages include drying, devolatilization, char burning, and smelt (molten inorganic matter) formation, with many of these processes overlapping in time and space. Normally, some devolatilization and most char burning and smelt formation occur after the droplet has fallen to the bottom of the boiler onto the char bed. A fraction of the droplets become entrained in the combustion gases of the recovery boiler and combust in suspension [2]. These droplets generally are initially 2 mm or smaller [5]. These particles and some fragments and vapors from the bed flow with the gases through the upper sections of the boiler, where they lead to deposit formation/flow constrictions or plugging and other operational problems. The particles react dynamically during flight, with large changes in temperature, composition, structure, and physical properties. The focus of this document is on the dynamic behavior of these particles.
Distinguishing Biomass Combustion Characteristics

Coal represents the dominant low-grade, ash-forming fuel by any measure—energy generation, mass consumption, CO₂ production, and economic influence. Consequently, a great many of the experimental techniques and theoretical approach used for many low-grade fuels, including biomass broadly and black liquor are usefully considered in the comparison to coal. This section discusses biomass broadly, with most of the discussion pertaining to traditional biomass (forest products, agricultural products, and residues) and to black liquor. While black liquor is a form of biomass and shares many of the characteristics discussed here with other biomass fuels, it is unique among even biomass fuels in important ways. This section is followed by another that discusses these unique combustion characteristics.

Table 1 summarizes the chemical compositions typical of several important classes of fuels. The relationships among these fuels appear most interesting when plotted as atomic ratios of hydrogen and oxygen to carbon (Figure 1). All individual data points in this figure represent sample results whereas the round, red, labeled data represent averages for the samples in each classification.

Black liquor exhibits both similarities and differences from other fuels. It is hydrogen poor compared to oils and other high-grade fuels, but not as hydrogen poor as coal. It is more oxygen rich than coal but less oxygen rich than biomass. It is lignin rich, as indicated by its position in comparison to lignin and cellulose on the figure and is obvious from the process from which it originates. Not evident from this figure is black liquor’s extremely high inorganic content, high initial moisture content, and generally fluid character. Also, owing mainly to high moisture, inorganic, and oxygen contents, it has a relatively low heating value compared to most other fuels. While each of these fuels exhibits its own interesting combustion characteristics, black liquor in many ways represents the most extreme fuel in terms of particle behavior. A few comments about the remaining fuels complete this section with an emphasis on traditional biomass fuels, whereas the bulk of this document focuses on the specific biomass fuel of black liquor.

Results of classical analyses of biomass and coal fuels reflect many, but not all, of the important differences in these fuels. Table 1 summarizes data from coal and biomass databases including several thousands of samples of fuels in various categories. As is seen, biomass differs from coal primarily in its higher oxygen, lower carbon, and lower sulfur content. Herbaceous biomass (grasses and straws) also contain much higher chlorine as a class than do either coals or woods. Some of these differences appear in Figure 1, where coal, biomass, black liquor, and a few other fuel compositions appear on a molar H:C to O:C ratio. Other important characteristics of biomass relative to coal include more widely ranging (0.1%-25%) ash contents, lower heating values (by about half on an as-delivered basis), much lower bulk energy densities (by more than an order of magnitude), generally higher alkali content for herbaceous biomass dominated by potassium, and substantially more fibrous and less friable character. Each of these characteristics lends specific characteristics to the fuels, only a few of which are discussed here.

Particle Size

Traditional biomass particle sizes of commercial interest typically range from 2-10 mm. This exceeds, for example, pulverized coal particle sizes and volumes by orders of magnitude. Biomass particles also exhibit highly aspherical characteristics and in this section size is characterized as the sphere-equivalent diameter, that is, the diameter of a sphere that has the same volume/mass of fuel as the biomass particle. There are several implications of this large size on biomass combustion, especially when compared to traditional coal combustion concepts. The focus here is on issues that impact practical system operation.

Table 1, Ultimate Analyses of Coal and Biomass Samples (compare with Table 2 for Black Liquor).

<table>
<thead>
<tr>
<th></th>
<th>Anthracite</th>
<th>Bituminous</th>
<th>Subbit.</th>
<th>Lignite</th>
<th>Grass</th>
<th>Straw</th>
<th>Wood Chips</th>
<th>Waste Wood</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>90.22</td>
<td>78.35</td>
<td>56.01</td>
<td>42.59</td>
<td>45.34</td>
<td>48.31</td>
<td>51.59</td>
<td>49.62</td>
</tr>
<tr>
<td>H</td>
<td>2.85</td>
<td>5.75</td>
<td>6.61</td>
<td>7.40</td>
<td>5.82</td>
<td>5.85</td>
<td>6.14</td>
<td>6.34</td>
</tr>
<tr>
<td>N</td>
<td>0.93</td>
<td>1.56</td>
<td>1.10</td>
<td>0.73</td>
<td>2.04</td>
<td>0.78</td>
<td>0.61</td>
<td>1.01</td>
</tr>
<tr>
<td>O</td>
<td>5.03</td>
<td>11.89</td>
<td>35.25</td>
<td>48.02</td>
<td>45.95</td>
<td>44.18</td>
<td>41.57</td>
<td>42.89</td>
</tr>
<tr>
<td>S</td>
<td>0.96</td>
<td>2.43</td>
<td>0.84</td>
<td>1.15</td>
<td>0.24</td>
<td>0.18</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Cl</td>
<td>0.03</td>
<td>0.08</td>
<td>0.01</td>
<td>0.01</td>
<td>0.62</td>
<td>0.70</td>
<td>0.02</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Figure 1. Comparison of biomass and coal on a molar H:C vs. O:C ratio

Figure 2. Visible-light images (left), temperature maps (center) and emissivity maps (right) of an approximately 2 mm diameter burning biomass (black liquor) particle/droplet.
Particle Shape

Quite independently of particle size, the unusual shapes of biomass particles also lead to more complex particle behaviors than commonly occur during coal combustion. Pulverized coal particles approximate spheres, with aspect ratios rarely exceeding 2. Biomass particle aspect ratios commonly exceed 6 and shapes more commonly resemble cylinders or plates/flakes than spheres. A sphere exhibits the smallest surface-area-to-volume ratio of any shape and therefore represents an extreme case in processes where such a ratio is important. Large particles commonly burn at or near diffusion-limited rates, which makes this ratio of paramount importance in predicting overall conversion times. Spheres, therefore, generally represent poor approximations for many biomass particles in combustion models.

Figure 3 illustrates the impact of particle shape on biomass combustion characteristics generally. This figure compares the measured and predicted mass loss profiles of relatively small (300 μm wood) biomass particles hand-sorted into different shapes. As indicated, the near-spherical biomass particles combust more slowly than the higher aspect ratio particles. Since both heat and mass transfer are dictated mainly by surface area for these large particles, the lower surface-area-to-mass ratios of spheres significantly decrease the overall combustion rate of these particles relative to less symmetric particles with the same total mass. Detailed discussions of the model and data on which these figures are based appear elsewhere [8, 9].

Experimental constraints limited these measurements illustrated in Figure 3 to relatively small particles. At more realistic biomass particle sizes the impact on particle conversion time becomes increasingly dramatic. Figure 4 illustrates the predicted ratio in overall conversion time for particles of various shapes as a function of sphere-equivalent size, with all times normalized to those of flakes. In the size range of greatest interest to many commercial biomass conversion facilities, the conversion times of the aspherical biomass particles change by factors of 2-3 relative to that of the spheres with the same mass. As indicated in the figure, this impact becomes increasingly less significant as particle size decreases, becoming relatively unimportant for pulverized coal particle sizes (100 μm and less). The single set of data indi-
Figure 3. Mass loss histories of sawdust particles with different shapes.

Figure 4. Conversion time vs. particle sphere-equivalent diameter for particles with aspect ratios of 5 (particles in inert – \(N_2\) – environments with 6 percent initial moisture with gas and radiative temperatures of 1050 and 1273 K, respectively). At higher aspect ratios, the ratio of conversion time increases (rises to approximately 3 for aspect ratios of 8 – which are common in biomass fuels).
Figure 5. Comparison of data and model predictions of an initial 9.5 mm droplet in a 1050 K inert gas (N₂)/1273 K radiative environment furnace in nitrogen (aspect ratio = 5, initial moisture 6 %, wood particle). The early temperature data in experiments 1 and 2 are biased because of conducting along thermocouple leads.
cated in this figure are based on the measurements illustrated in Figure 3. Many additional data have since been collected that confirm the predictions of Figure 4 over a broader size range.

**Moisture and Volatiles Contents**

The shape, size, and relatively high moisture and volatiles contents of biomass particles and especially black liquor droplets influence conversion histories in practical ways. Figure 5 illustrates predicted centerline and surface particle temperature histories compared with measured particle temperatures. The interior data come from a thermocouple imbedded in an approximately 9.5 mm initial diameter biomass particle. Model comparisons for similar data from biomass and black liquor particles/droplets ranging from < 1 mm to > 10 mm and a detailed description of the model appear in the literature [8-17]. Some particles and especially black liquor droplets distort wildly during combustion, in which cases there is no practical way of knowing where the thermocouple bead is relative to the droplet center during the experiments, but video records confirm that it remains inside the droplet somewhere, so its results are considered interior temperatures. The data shown here involve less wildly contorting particles and thermocouple readings that more reliably indicate a center temperature as opposed to an interior temperature.

The figure indicates that the center of the droplet remains wet and vaporizing well after the surface reaches devolatilization temperatures, as indicated by the low and sub-boiling predicted center temperature coinciding in time with surface temperatures over 700 K. Note that biomass and black liquor particles begin devolatilization and swelling at lower temperatures than do coal particles, mostly due to the overall lower molecular weight of their condensed-phased organic constituents. Heat conduction along the thermocouple leads bias the early temperature data in Experiments 1 and 2 to high values – a problem largely avoided in Experiments 3 and 4 by running the leads along the axial rather than the radial direction of these cylindrical particles. Larger droplets/particles and higher heating rates (these data come from a 1050 K gas/1273 radiative environments in an inert N₂ environment) generate larger temperature gradients still. Predicted composition plots confirm this inference from the temperature, but we have yet to devise means of generating anything other than overall mass loss with which to confirm such predictions. The interior temperature measured by the thermocouple generally lies between the predicted surface and center temperatures as would be expected. The measured temperature overshoot centered around 5 s residence time may arise from some residual oxygen in the nominally nitrogen-purged furnace in which these experiments occurred, or it may relate to exothermic devolatilization reactions that occur during the latter stages of devolatilization.

In addition to the water-vaporization-related temperature plateau seen at the particle center, the rapid volatile loss also impacts temperature rise. Under the relatively mild conditions of these experiments, this impact is subtle and is largely responsible for the departure of the observed temperature rises from smooth exponential-like profiles that would exit in the absence of such blowing effects. However, under more severe conditions, the volatile yields and especially the combustion of such volatiles in the particle boundary layers have pronounced impacts on particle temperature histories.

These process combine to produce particle off gas compositions and particle reaction timelines that differ substantially from those that would be predicted if biomass particles were treated as large, low-density, coal particles using traditional modeling techniques.

There are additional considerations associated with transformations of particle inorganic material into fly ash and its subsequent impact on deposition, corrosion, SCR performance and fly ash utilization. These considerations will appear in other documents.

**Distinguishing Black Liquor Combustion Characteristics**

Black liquor is unique among major low-grade fuels in amount and composition of inorganic species that it contains. As can be seen from Table 2, black liquor consists of about 20% sodium. About half of this sodium is in the form of inorganic salts, and the other half is in the form of acidic functional groups such as carboxylates and phenolates [18]. During combustion, black liquor generates sodium-containing vapors that, in turn, form submicron-sized inorganic particles or aerosols. These particles, known as fume, contain sodium carbonate (Na₂CO₃), and sodium sulfate (Na₂SO₄) with smaller amounts of sodium chloride (NaCl) and other sodium- and potassium-containing species. Fume formation depends strongly on furnace temperature and furnace oxygen content [2].
experiments indicate that the majority of fume forms from entrained black liquor particles while some forms from the sub-stoichiometric char bed or smelt in the bottom of the boiler [19].

<table>
<thead>
<tr>
<th>Table 2. Typical Black Liquor Composition [9].</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element</strong></td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>Cl</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td><strong>Other</strong></td>
</tr>
</tbody>
</table>

Other unique characteristics of black liquor fuels include: (1) while highly viscous at room temperature, black liquor is a relatively easily handled fluid at process temperatures (near 100 °C), unlike most highly ash-laden fuels such as traditional biomass and coal; (2) black liquor swells more than any other common fuel during combustion, commonly experiencing density decreases of one to two orders of magnitude; (3) black liquor in recovery boiler applications forms (by design) droplets of nominally 2 mm, well above pulverized coal sizes (typically 45 micron average, 100 micron top size) and similar to entrained-flow biomass particle sizes (typically 1-6 mm); (4) the inorganic material in black liquor participates dynamically in carbon conversion and other important aspects of liquor combustion to a much greater extent than the inorganic material in either coal or traditional biomass; and (5) black liquor composition and organic structure differ from traditional biomass and coal (discussed later in more detail), for example with overall oxygen content that lies between that of coals and traditional biomass as a group and a hydrogen content greater than coal and comparable to many traditional biomass fuels. This document details many of these aspects of black liquor combustion.

The current investigation focuses on the black liquor droplets entrained by flue gases that react in suspension in the recovery boiler. As shown later, both the inorganic content of the liquor and the substantial swelling that occurs during combustion dramatically affect these droplets. The investigation includes both experimental and modeling efforts of single particle combustion. Both the experimental data and the model give insight into the reaction rates and mechanisms.

**Highlights of Previous Investigations**

This section summarizes results from investigations related to this topic. It also includes a critical review of the work done by this laboratory, notably by Le-ong Teng “Elvin” Ip, who previously worked on this project and whose techniques are largely adapted in this work. Ip’s work appears in his dissertation, Comprehensive Black Liquor Droplet Combustion Investigations [6] and elsewhere [6,7,10,13,14,16]. His investigations included experimental work on black liquor droplets to obtain data on droplet size, shape, internal and surface temperature, and mass loss during combustion and pyrolysis. This review also highlights work done outside this research group. A numerical model of black liquor droplet combustion quantitatively predicts similar data, based largely on related work conducted by Hong Lu focusing on biomass particles. During his investigation, Ip also obtained qualitative and quantitative data of intermediate sized particle (ISP) formation. Aside from the investigation of ISP formation, the current document improves considerably on the data model pioneered by Ip and Lu.

**Droplet Combustion Experiment**

Many different techniques characterize black liquor combustion and pyrolysis. The technique of most importance to this work is single particle combustion and pyrolysis. Hupa et al. [20] pioneered this work. They studied black liquor particles by suspending them on a thin platinum wire or on a thermocouple and placing them in a muffle furnace. By placing the black liquor droplet on a thermocouple, they measured the internal droplet temperature during the burn. They also used a video camera to record the burning droplet and measure particle size and burning times. Frederick et al. used a two-color pyrometer to measure the surface temperature of the particle during combustion and pyrolysis [21]. Ip used a similar technique except that his furnace gases were not stagnant [16]. He also incorporated a mass balance to measure particle mass during burning. The main disadvantage to this technique is that the wire on which the droplet rests can significantly impact the heat transfer to the particle.

**Molecular Beam Mass Spectrometry**

A single particle reactor [22] provides time-resolved, simultaneous data on surface temperature, internal temperature, mass, and composition during biomass drying, devolatilization, and char
oxidation/gasification biomass particles. Figure 1 schematically illustrates the experimental facility for the single particle combustion study.

Single biomass particles suspended on a type-B or type-K thermocouple and connected to a wireless data logger, from PACE Scientific, provide internal temperature data at a speed of 20 Hz. The data logger, thermocouple, and the biomass particle, sit on a balance, which provides dynamic mass loss data. For sufficiently large particles, a hole the size of the thermal couple wire drilled through the center the particle for thermocouple suspension provides access thermocouple access to the particle interior. Mass loss data from the balance with a resolution of 0.1 mg and temperature data from the thermocouple simultaneously stream to the data acquisition system. An imaging system and optical pyrometer records the physical changes and spatially resolved surface temperature distribution of the reacting biomass particle. Alternatively or additionally, a surface thermocouple records the surface temperature at a point. A molecular beam mass spectrometer (MBMS), specially constructed at BYU, samples off gases from the particle to determine composition. In combination, these systems provide time-resolved measurements of internal temperature, surface temperature, mass, shape, size, and off gas composition simultaneously during particle reaction. This single particle reactor produces experimental data, including mass loss, surface and center temperature, as functions of time for poplar dowel particles during drying, pyrolysis, and char oxidation/gasification processes.

The distinguishing feature of the MBMS relative to other mass spectrometers is its sampling port. The MBM sampling port usually consists of a series of two or three nozzles or skimmers. The inlet orifices to each of these nozzles cause choked flow behavior. The gases expand nearly adiabatically through a shock wave. In well-constructed nozzles, this expansion causes significant cooling and decreases internal energy. This cooling rapidly quenches the gases and minimizes reactions. The decrease in internal energy causes the molecules to be more resistant to fragmentation after being ionized [23]. The series of orifices decrease the pressure of the system to the appropriate operating conditions of the mass spectrometer ($10^{-5}$-$10^{-8}$ Torr). Thus the series of orifices allows near-real-time and essentially in situ sampling of combustion or pyrolysis gases into the mass spectrometer. This series of inlet skimmers, if properly aligned, allows condensable species to remain in the gas phase at temperatures well below their condensation temperatures because of the absence of nucleation surfaces [24]. Figure 6 shows a diagram

Figure 6, Single particle reactor schematic diagram.

*: View ports are in three orthogonal directions
of the double skimmer assembly used at BYU. In this configuration, both skimmers create choked-flow, adiabatic expansion of the gases. If the centerlines of both are aligned, the molecules emitted from the second are all traveling in nominally the same direction at near sonic-velocities and form a beam of molecules, that is, a molecular beam [8, 14, 17].

Ip’s group had significantly modified an electro-spray mass spectrometer to meet the requirements of the MBMS. These modifications included changing the electro-spray ion source to an electron impact ion source, rewiring the mass spectrometer for the new source, adding power supplies, cutting and welding a new flange onto the mass spectrometer vacuum chamber, updating the data system, and rebuilding parts of the skimmer assembly [14].

The benefits of using such a mass spectrometer are limited. The mass spectrometer is a semi-quantitative instrument because many factors influence the mass spectra. These include operating pressure, electron energy, quadrupole tuning, and the ion source. Electron energy affects ionization efficiency and ion fragmentation. In tuning the quadrupole, trade-offs between signal intensity and spectral resolution force some compromises in each. These variables make it difficult to get absolute species concentration from the mass spectrometer, requiring difficult calibrations of the mass spectrometer at the conditions used in the experiments. However, a mass spectrometer can measure relative change in species concentration versus time easily and accurately [23].

Swelling During Drying and Devolatilization
Black liquor dramatically swells during drying and devolatilization [16, 25]. The gases created upon heating the black liquor create bubbles that expand or inflate the particle. This swelling drastically impacts particle heating rates, drag/trajectory, mass transfer, and reaction rates. Various investigations indicate what variables impact the extent of droplet swelling. The most important of these variables is reportedly the lignin to carbohydrate ratio. Black liquor experiences maximum swelling around a ratio of 50/50. Black liquor swelling decreases irreversibly when its pH decreases by adding acid [26]. Wintoku et al. proposed a swelling model based on first principles, yet their model was not consistent with data [27-29].

Flame Region Surrounding a Droplet
Flame models based on mass and energy balances commonly assume complete or partial combustion, usually infinite kinetics, and commonly constant or average diffusivities in the flame layer [30-32]. These assumptions allow computation of heat and mass fluxes from the devolatilizing particle. When implementing this type of model, one must assume whether the flame is present or not. Verrill et al. assumed that a flame was present when the Reynolds number was less than one [34]. Järvinen’s model uses a flame model when the Damkohler number exceeds three [33].

Bryden used a different approach to solving the flame layer problem [35,36] The domain of the control volume extends into the gas phase, includ-
ing a stagnant film boundary layer. In the outermost shell, the concentrations of the gas species and the temperature equal the bulk gas conditions. In this approach, the flame reaction kinetics and mass transfer clearly indicate—from the high temperature and decreased oxygen content in the film layer—whether a flame is present or not. One of the major variables in this approach is the film thickness, or the distance from the droplet surface to the bulk gas. Mass and heat transfer decrease with increasing film layer thickness. Bryden did not explain how he determined the boundary layer thickness.

**Inorganic Chemistry**

Inorganic species play an important role during black liquor combustion. They aid in char conversion, capture gas-phase sulfur species, and ultimately account for much of the fouling in a recovery boiler. Inorganic species are the major component of fume and intermediate sized particle (ISP), which conglomerate and ultimately account for the deposit formation in a boiler [37-39], which depends strongly on furnace temperature and oxygen content [26]. Black liquor is typically about 20% sodium and 1% potassium. Although most investigations have concentrated on sodium species, it is generally assumed that potassium species follow the same mechanisms as their sodium equivalents. Furthermore, combinations of sodium and potassium or of chlorides and sulfates form eutectics and other solutions that impact both deposition rates and deposit properties. Of the inorganic species, sulfates and carbonates form the largest fractions. Included with Equations (1) and (2) are the molar heat of reaction, \( \Delta H_{rxn} \), and the molar Gibb’s energy of reaction \( \Delta G_{rxn} \) for reference.

**Sulfur Containing Inorganic Species**

Black liquor typically contains about 4% sulfur. Of this sulfur, initially about 40% is sulfate, 35% is thiosulfate, and 25% is organic sulfur. Thiosulfate decomposes almost immediately upon heating and thus is not an active participant during the rest of the combustion process. The organic sulfur forms \( \text{H}_2\text{S} \) and \( \text{COS} \), but can be recaptured through reactions with different fume species [40-42]. Sulfate acts as a carbon conversion catalyst through a mechanism referred to as the sulfide/sulfate cycle (Reactions (1) and (2)). These reactions are extremely important in the char bed where simultaneous sulfate reduction and carbon oxidation are essential [3,43]. In a reducing environment sulfide is more thermodynamically stable than sulfate; however, in an oxidizing environment the opposite is true.

**Carbonates**

In an investigation on fume formation, Li and van Heiningen studied the decomposition of sodium carbonate in black liquor under different environments. They observed that carbon reduces carbonate and that this process releases sodium vapor, Reaction (3). They were able to obtain a kinetic rate expression in a nitrogen environment. They

\[
\begin{align*}
\text{Na}_2\text{S} + 2\text{O}_2 & \rightarrow \text{Na}_2\text{SO}_4 \quad \Delta \tilde{H}_{\text{rxn,25 } ^\circ \text{C}} = -1020 \frac{\text{kJ}}{\text{mol}} \\
\Delta \tilde{G}_{\text{rxn,1000 } ^\circ \text{C}} &= -886 \frac{\text{kJ}}{\text{mol}} \quad \Delta \tilde{H}_{\text{rxn,1000 } ^\circ \text{C}} = -982 \frac{\text{kJ}}{\text{mol}} \\
\frac{(2-f)}{2} \text{Na}_2\text{SO}_4 + 2\text{C} & \rightarrow \frac{2-f}{2} \text{Na}_2\text{S} + 2 \cdot f \cdot \text{CO} + 2 \cdot (1-f) \cdot \text{CO}_2 \\
\text{where} & \quad 0 \leq f \leq 1.0 \\
\Delta \tilde{G}_{\text{rxn,1000 } ^\circ \text{C}} &= -270 \frac{\text{kJ}}{\text{mol}} \quad \Delta \tilde{H}_{\text{rxn,25 } ^\circ \text{C}} = 200 \frac{\text{kJ}}{\text{mol}} \\
\Delta \tilde{G}_{\text{rxn,1000 } ^\circ \text{C}} &= 239 \frac{\text{kJ}}{\text{mol}} \quad \Delta \tilde{H}_{\text{rxn,1000 } ^\circ \text{C}} = 1130 \frac{\text{kJ}}{\text{mol}} \\
\text{Na}_2\text{CO}_3 + 2 \cdot \text{C} & \rightarrow 2 \cdot \text{Na} + 3 \cdot \text{CO} \quad \Delta \tilde{H}_{\text{rxn,25 } ^\circ \text{C}} = 1240 \frac{\text{kJ}}{\text{mol}} \quad \Delta \tilde{G}_{\text{rxn,1000 } ^\circ \text{C}} = 239 \frac{\text{kJ}}{\text{mol}}
\end{align*}
\]
observed that both CO and CO₂ suppress sodium carbonate decomposition, but did not acquire reaction kinetics for the decomposition reaction when these species are present [44,45]. Gairns et al. found that sodium carbonate decomposition increased sharply between 800-900 °C, but disappeared entirely by introducing 15% CO₂ at 900 °C [46]. In addition to sodium release due to sodium carbonate decomposition, Frederick and Hupa found that between 23-35% of the sodium is released during pyrolysis [47]. Others later proposed that this sodium release is due to small particles being ejected from the droplets [48].

Motivation for this Document

The current investigation builds upon the work of the research mentioned previously in this section. This investigation incorporates both modeling techniques as well as single droplet experiments to understand the mechanisms of black liquor droplet combustion. This document outlines two types of single droplet experiments. These experiments utilize techniques similar to those developed previously, including work with a molecular beam mass spectrometer, using thermocouples to measure internal droplet temperature during combustion, and a pyrometry technique to measure surface temperature. In addition to these techniques, this project developed new techniques for surface temperature measurement, mass measurement, and data synchronization.

The model developed during this investigation incorporates various sub-models to account for the phenomena explained in this section. This document explains how the model quantifies swelling of black liquor, the sulfate/sulfide cycle, carbonate decomposition, and the presence of a flame. By using both experiments and modeling, this investigation reveals some of the important mechanisms of black liquor combustion.

Experimental Approach

The experimental portion of this project involved substantial experimental design and troubleshooting. Experimental facilities used in this project include purchased equipment (cameras, temperature data logger, temperature controllers, and relays), newly designed and constructed equipment (single-particle furnace), rebuilt equipment, the last category including an MBMS built from portions of an abandoned, non-molecular-beam mass spectrometer and a spare detector. This section summarizes the experimental methods and the features of the equipment used in the project.

Experimental Materials and Methods

Five liquors formed the suite of fuels used in this project. Their compositions are indicated in Table 3. These liquor samples were all from industrial paper mills.

The first two liquors, A and B, are softwood liquors and come from a mill in the Northwest United States. Liquor A came with very high solids-content (>95%), and Liquor B came with about 50% solids. The other three liquors, C, D, and E, were softwood/hardwood mixed liquors and came from different mills. Liquor C came with 55% solids, Liquor D came with about 70% solids, and Liquor E came with 77% solids. All liquors were concentrated to at least 70% solids content prior to use. Two types of experiments comprise the experimental portion of this project: droplet combustion experiments and MBMS experiments. In the droplet experiments, drying increased the black liquors B and C to about 70% solids content while the other liquors remained at the concentrations shown in Table 3.

Droplet Combustion Experiment

The first type of experiment was a droplet com-
bustion experiment. The equipment used in this experiment includes a furnace built at BYU (Figure 8), three SVS Vistek CCD cameras, a Pace Scientific XR440 Pocket Logger and associated thermocouple (for internal temperature measurement), a Scientech SA 310 mass balance, and a Thermolyne 21100 tube furnace (used to preheat the gas). The furnace is equipped with six view ports oriented in three orthogonal directions. These view ports are for video and pyrometry imaging. They are all viewed in the same plane in the figure to better illustrate the furnace construction, but in fact the axis of the horizontal port is perpendicular to the page.

Four silicon carbide electrical resistance-heating elements from Kanthal Globar positioned at the bottom of the furnace heat the furnace. A K-type thermocouple provides feedback to a Watlow 5-10 V controller and two Continental solid-state relays to control the 110 V potential to heating elements. The system includes a water-cooled jacket that slides into the middle of the furnace to provide a shielded environment for the particles during setup. Two rotameters control the gas flow to the furnace, one manufactured by Cole Palmer and the other by Dwyer. A mass flow meter calibrates both. The cameras, the mass balance and the pocket logger connect to a single computer for synchronization purposes. More detailed descriptions of the furnace, the mass balance, and the cooling jacket, as well as a novel technique of using video imaging from a single camera for pyrometry measurement, appear in Ip’s dissertation [13,16].

During each experiment, a 1.5 – 4 mm black liquor droplet suspended on a thermocouple burned in the furnace. Simultaneous collection of so many parameters complicates the experimental procedures and makes each experiment somewhat tedious, but the procedures provide unique and comprehensive data. The temperature measurement recorder did not connect directly to the computer (by design).

Typical experiments proceeded as follows: A weighed droplet was placed on an approximately 0.01 inch diameter type K thermocouple. The thermocouple was attached to the temperature logger and positioned in the balance. The thermocouple-droplet assembly rolled toward the furnace until the droplet reached the center of the furnace, inside the water-cooled jacket. After the mass balance oscillations stopped, mass measurement and camera measurement were initialized, and the cooling jacket was pulled from the furnace.

* The three viewports are in three orthogonal direction

Figure 8. Setup for the Droplet Combustion Experiment.
With the cooling jacket removed, the droplet almost immediately experiences the hot gases of the furnace. The droplet then dries, and either pyrolyzes in an inert environment or devolatilizes and oxidizes in an oxidizing environment. Experiments include runs in both air and nitrogen environments. During each experiment, the data logger records temperature at a rate of 20 Hz; The mass balance recorded mass at 18-19 Hz; The camera’s images were stored at about 15 Hz.

After the droplet finishes reacting, the particle mass and internal temperature data download to a spreadsheet. The pixel counts across the particle’s horizontal and vertical lengths determine the particle sizes. The known view point tube diameter serves to calibrate these measurements. Because the droplet is located midway between the two view point tubes, the scaling factor for the droplet is simply the average of scaling factors calculated for the two view point tubes. This document reports geometric mean diameters, that is, the square root of the product of the horizontal and vertical lengths of the particle. The surface temperature measurements come from two points on the particle surface. At the beginning of a run, these data may be far from representative or random, because the pyrometry technique as a lower detection limit of approximately 600 °C. Both surface temperature and size data have 0.5 Hz temporal resolution.

Optical Pyrometer and Color-Band Method

The Color-Band Method for optical pyrometry was developed by Lu and Ip, and a detailed explanation of this method is given by Ip [7,13,14]. Typically, a CCD camera filters light into four colors that report to red, blue, and two green pixels. Lu and Ip developed Equation (4), which describes how the camera’s pixel value, DN, relates to the temperature based on a few simplifying assumptions, where DN is the digital number describing the intensity of one color of light. The sensitivity of each type of sensor can be described as a function of wavelength by a function called the spectral responsivity, S(λ). The emissive power per unit wavelength, E(λ,T), of an object is described by Plank’s Law, where E(λ,T) is the product of the surface emissivity and the blackbody radiation per steradian. The pixel value is the integral of the product of E(λ,T) and S(λ) times the lens and camera setting factors, Equation (4). In Equation (4), τ is the lens transmission factor, D is the lens diameter, d is the distance between the object and the sensor, a is the pixel area, X is the magnification, and t is the camera exposure time. The technique takes advantage of multiple color bands to simplify the measurement. By taking the ratio of the pixel values for different color sensors, the lens and camera setting factors cancel in the equation, Equation (5).

The main advantages of this technique include accuracy, relatively high signal to noise ratios because of the integrations, inexpensive equipment, and simple implementation. One of the major drawbacks for combustion application is that flames that surround an object interfere with the temperature measurement. This is not unique to color-band pyrometry. Two- and single-color pyrometries also may not penetrate the flame layer to obtain a surface temperature [21].

Results and Discussion: Droplet Combustion

This section discusses the experimental results of the single droplet combustion experiments. Experiments yielded insight into interactions between droplet swelling, mass loss, and temperature changes. Observations also show mechanisms that will be important in modeling, especially a surface char “regeneration” mechanism.

\[
DN = \frac{\pi D^2 a^2}{4 d^2 X} \Delta t \int_{\lambda_1}^{\lambda_2} S(\lambda) E(\lambda, T) d\lambda
\]

where \[ E(\lambda, T) = \varepsilon \frac{c_1 \lambda^{-5}}{c_2 e^{\frac{c_1}{\lambda T}} - 1} \]

\[
\frac{DN_G}{DN_R} = \int_{\lambda_1}^{\lambda_2} \frac{S_G(\lambda) E(\lambda, T) d\lambda}{\int_{\lambda_1}^{\lambda_2} S_R(\lambda) E(\lambda, T) d\lambda}
\]

(4)
Simultaneous Mass Loss, Size, Internal and Surface Temperature

The experimental data collected offer many insights into the combustion behavior of black liquor. Figure 9 shows the results from a 45-mg black liquor A droplet in 750 ºC air. The droplet’s size changes significantly during the combustion process. The droplet’s radius increases rapidly during drying and especially devolatilization. Afterwards, the droplet shrinks as the char burns out.

The thermocouple temperature curve shown by pink squares ascends quickly at first, up to a plateau at about 130 ºC. Water evaporation from this salt-saturated fuel leads to this plateau. After the water evaporates from the droplet, the temperature again increases. Initially the temperature increases slowly; the gases that are evolved during devolatilization decrease the heat transfer to the particle. Also, local gas evolution in the particle decreases heat transfer locally. Once devolatilization is complete, the temperature increase is more rapid due to the combined effects of no gas evolution, smaller mass and larger surface area. The center temperature increases to a maximum near the end of char burning. This maximum temperature measured by the thermocouple usually corresponds closely with the time that the smelt bead collapses onto the thermocouple. The temperature then drops slowly to a steady-state temperature in the furnace somewhere between the local gas and furnace wall temperatures. This temperature decrease is slow for two reasons. First, by this point the particle has shrunk to its smallest volume, thus the smallest surface area. Second, exothermic sulfide oxidation reactions continue after char burning, further slowing the temperature change.

Similar mechanisms affect the mass loss. Mass loss during drying is slower than during devolatilization. Devolatilization causes the most rapid mass loss. Char burning, associated with a slower mass loss, follows devolatilization. The surface temperature measurements come from two points. The cameras can only accurately determine high temperatures (> 600 K). This means that during the early stages of combustion, only temperatures above this limit are reported. While some region of the surface seems nearly always to have ignited and be burning at this limit, the early temperatures are highly non-representative of the overall droplet surface temperature. The temperature measurements tend to show that although there is a large variance in the surface temperature, the maximum surface temperature tends to stay nearly constant throughout most of the combustion process. Some of the reported surface temperatures may have been affected by flame interference.

Another phenomenon revealed by the surface temperature measurement is the beginning of char burning on the surface. As shown in Figure 9, for a very dry black liquor droplet (95% solids), surface char burning starts while the internal temperature of the particle is still near the boiling point of water. This creates very large temperature gradients inside the droplet of at least 280º C/mm. The surface temperature measurement is always higher than the thermocouple-measured internal temperature, even as the droplet reaches a pseudo-steady combustion regime. This is likely due to the thermocouple leads being cooled by the ambient gases. Because the thermocouple leads are exposed to the surrounding gas, the leads conduct heat away from the thermocouple bead, decreasing the temperature measurement.

After the initial shrinking of the particle, the particles shown in Figure 9 and Figure 10 swell again. This secondary swelling may indicate that there is

Table 4, Experimental Runs

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Liquor Type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
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<tr>
<td>Solids Content (%)</td>
<td>70</td>
</tr>
<tr>
<td>Initial Mass mg</td>
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</tr>
<tr>
<td>Particle Volume 10⁵ m³</td>
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</tr>
<tr>
<td>Velocity m/s</td>
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</tr>
<tr>
<td>Max TC Temperature ºC</td>
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</tr>
<tr>
<td>Gas Temperature ºC</td>
<td>715</td>
</tr>
<tr>
<td>Avg. Peak Swelling (r/rₘₐ)</td>
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</tr>
<tr>
<td>Drying Time (s)</td>
<td>7</td>
</tr>
<tr>
<td>Devolatilization Time (s)</td>
<td>17</td>
</tr>
<tr>
<td>Total Combustion Time (s)</td>
<td>22</td>
</tr>
</tbody>
</table>

TC is thermocouple. *Thermocouple may have come out of droplet
Figure 9. 44.8 mg Droplet of Black Liquor A in 750 ºC Air, Gas Velocity=0.35 m/s, 95% Solids.

Figure 10. 23.2 mg Droplet of Black Liquor A in 800 ºC Air, Gas Velocity=0.367 m/s, 95% Solids.
residual char or black liquor solids when the smelt collapses onto it. The smelt reactions with the residual char release gases, expanding the particle once again.

Figure 10 and Figure 11 show similar trends to those described above. The droplet in Figure 11 has a higher moisture content (70% solids). This leads to a later initial char burning time compared with the droplet of Figure 10. The droplet in Figure 10 started char burning after only about 1 ½ seconds. There was an interesting mass increase at the char burning shown in Figure 10. Although this may only be a result of turbulence around the particle, it raises the question of how much mass increase might result from sulfide oxidation during smelt oxidation. It is likely that the mass of the particle increases during smelt oxidation.

A summary of some of the main combustion characteristics for six runs appears in Table 4. The reported times for drying, devolatilization, and total combustion time are approximate since there was significant overlap of the stages of combustion.

**Video Observations**

Video images reveal further information on combustion mechanisms. Video images during drying and devolatilization reveal that particle conditions are highly two- or three-dimensional. This particular furnace is bottom heated and has a constant gas flow around the particle. During devolatilization, a bright orange-yellow flame develops near the droplet as shown in Figure 12.

During devolatilization, the droplet becomes very porous. Char burning exposes these large voids. As the char burns, the remaining smelt forms beads that agglomerate on the droplet surface. As char burning continues, the smelt beads grow by agglomeration. This agglomeration seems to minimize the mass- and heat-transfer barrier that the smelt may have imposed if it did not agglomerate. This means that instead of oxidizer having to dif-
fuse through a thin stagnant layer of a smelt to penetrate to the char; the char is constantly exposed on the surface. This has significant modeling implications as discussed later. This mechanism for exposing new char to the surface is called the char regeneration mechanism. Figure 13 illustrates this mechanism. It shows how a large void opens near the center of the droplet and eventually exposes new char on the surface.

As the droplet completes char burning, smelt agglomeration exposes large voids in the particle center formed during devolatilization. The size of these voids is roughly the same order of magnitude as the entire particle. This mechanism may greatly aid the speed of char burning because it allows surrounding gases to enter close to the center of the particle. The structure of the droplet may also add to the turbulent convection around the particle, hence aiding mass transfer.

At oxidation temperatures, the particle’s interior structure melts. The droplet begins to collapse upon itself and agglomerate into one large bead. Thus, the opening of large voids in the center of the particle may result in a rapid volume change, such as appears in Figure 9. When the droplet collapses, the unburned char reacts with liquid sodium carbonate and sodium sulfate, causing rapid gas release.

---

Figure 13, Successive Images during Char Burning, 26.6 mg Droplet of Black Liquor E in 650 °C Air, 0.32 m/s Gas Velocity, 70% Solids. (Numbers Indicate Total Elapsed Burn Time).

Figure 14, Large Voids during Char Burning, Very Large Droplet of Black Liquor A, 95% Solids, in 800 °C Air.
This rapid gas release may be the cause of intermediate sized particles being ejected. Near the end of char burning, the droplet releases burning intermediate sized particles (ISP) easily seen by the cameras. Although these particles occasionally appear throughout most of the combustion process, Figure 15 shows the spectacular event that sometimes characterizes the end of char burning. This large release of ISP is consistent with Ip’s observations. Lien et al. observed that in char beds ISP formation increases with bed temperature [49,50]. In their experiments, increasing inlet oxygen concentration increased bed temperature. Increased oxygen on the bed could oxidize inorganic species. Thus, their results may also point toward ISP formation from a reaction of oxidized inorganics with char.

Ip et al. also found that increasing the moisture content of the liquor decreased the ISP formation [7,10,13]. Increased moisture content leads to increased auto-gasification. During gasification, no oxygen is present in the char layer, and the sulfate/sulfide cycle is broken because the sulfide does not oxidize back to sulfate. This decrease in oxidized inorganic species could be the cause of decreased ISP formation in initially wet particles. The two pictures in Figure 15 record the same particle at the same time using identical cameras and lenses but with different aperture settings. The left image shows only one particle leaving the droplet, but the other image shows hundreds of particles leaving the droplet. The right image indicates the particle is nearly exploding. The left image indicates only minor surface reactions occurring. (However, if the left image is manipulated, such as inverting the colors as in Figure 16, more particles can be seen.) The distinct difference between these two images illustrates how difficult ISP ejection may be to quantify using visual approaches. Conclusions derived from visual observations that more ISP form at higher temperatures should be highly suspect. Being able to see the ISP depends strongly on their temperature and camera set-

Figure 15, ISP Ejection After Char Burning, Two Simultaneous Images, Large Droplet of black Liquor A, 95% Solids, in 800 ºC Air.

Figure 16, ISP Ejection After Char Burning, Very Large Droplet of Black Liquor A, 95% Solids, in 800 ºC Air (Colors Inverted).
tions. Ejection at lower combustion temperatures or during the early stages of combustion would therefore be more difficult to validate visually due to the cooler temperature of the ISP.

**Droplet Model Description and Development**

Modeling combustion processes entails solving transport equations [51], Equations (6), (7), and (8), using a control-volume method [52]. The model calculations reported here result from modifications of a code that was originally developed for biomass particle combustion written primarily by Lu and partially by Ip [16]. Many simplifications had to be made to the model because of incomplete understanding of all of the mechanisms and kinetic parameters required by a highly detailed model as well as for computation time considerations. Nevertheless, even the simplified model provides significantly more detail than those commonly used to describe black liquor combustion. This one-dimensional, transient model describes heat and mass transfer and species continuity for arbitrary shapes. The model uses the power-law scheme to solve the combined advection-diffusion problem. The term “advection” in this document describes flow in the radial direction. Darcy’s law for flow through a porous medium and the continuity equations quantifies this flow, with the numerical solution using the SIMPLE (Semi-implicit Method for Pressure Linked Equations) algorithm [52]. The model predicts transient temperature, velocity, pressure, composition, reaction rate, mass- and heat-transfer rates, and related data as a function of one spatial dimension. This dimension is the radius in the case of spherical particles and the equations use \( r \) for the independent variable describing it.

The integer variable \( n \) changes with the coordinate system that best describes the shape and ranges from 0 to 2. For example, a sphere corresponds to a value of two for \( n \). This enables the code to perform calculations for other shapes. Because of swelling during black liquor combustion, the internal radiation heat transfer becomes important. The solid-phase thermal conductivity of black liquor, \( \lambda_S \), depends on temperature and composition as indicated in Equation (9) [26].

\[
\frac{\partial}{\partial t} \varepsilon \rho_g Y_i + \frac{1}{r^n} \frac{\partial}{\partial r} \left( r^n \varepsilon \rho_g Y_i u \right) = \frac{1}{r^n} \frac{\partial}{\partial r} \left( r^n \varepsilon D_{eff,i} \varepsilon \frac{\partial Y_i}{\partial r} \right) + S_i \tag{6}
\]

\[
\frac{\partial}{\partial t} \left[ \sum_i \rho_i \hat{H}_i + \sum_k \rho_k \hat{H}_k + \varepsilon \rho_g \sum_j Y_j \hat{H}_j \right] + \frac{1}{r^n} \frac{\partial}{\partial r} \left[ r^n \varepsilon \rho_g u \sum_j Y_j \hat{H}_j \right] = \frac{1}{r^n} \frac{\partial}{\partial r} \left( r^n \lambda_{eff} \varepsilon \frac{\partial T}{\partial r} \right) + \frac{1}{r^n} \frac{\partial}{\partial r} \left[ r^n \left( \rho_g \varepsilon \sum_j D_{eff,j} \frac{\partial Y_j}{\partial r} \hat{H}_j + D_{eff,k} \frac{\partial \rho_k}{\partial r} \hat{H}_k \right) \right] \tag{7}
\]

where,

\[
\hat{H}_i = \hat{H}_i^0 + \int_{T_0}^{T} C \rho_i(T) dT, \text{ } \text{ } i \text{ is any species involved}
\]

\[
\frac{\partial \rho_g}{\partial t} + \frac{1}{r^n} \frac{\partial}{\partial r} \left( r^n \varepsilon \rho_g u \right) = S \tag{8}
\]

\[
\lambda_S = (1.44 \times 10^{-1} \cdot (T - 273.15) + 0.58 - 0.335 \cdot Y_s) \frac{W}{m K} \tag{9}
\]
Temperature, $T$, is in Kelvins, and $Y_s$ is the mass fraction of the solids. This conductivity combines with the conductivity of the gas, $\lambda_g$, and radiative properties to form an effective thermal conductivity which, when using a diffusion approximation for cubic pores and an opaque cube pore model, is expressed as in Equation (10) [53].

$$
\lambda_{\text{eff}} = \lambda_s \left(1 - \varepsilon^{2/3}\right) + \frac{\varepsilon^{2/3}}{1 - \varepsilon^{1/3}} \left(\frac{1}{\lambda_s} + \frac{\varepsilon^{1/3}}{\lambda_g}\right) + \frac{16\sigma T^3}{3a_R \varepsilon}
$$

A value of 850 m$^{-1}$ for $a_R$, known as the Rosseland mean absorption coefficient, was given by Järvinen based on a sensitivity analysis [53]. The pressure outside of the particle is assumed constant at ambient pressure; thus, to find velocities, in the boundary layer only the continuity equation is solved. Equation (11) is Darcy’s Law, where $\mu$ is the gas viscosity, $\eta$ is the permeability, and $P$ is pressure.

$$
u = -\frac{\eta}{\mu} \frac{\partial P}{\partial r}
$$

$$
Nu = 2.0 + 0.6 \cdot Re^{1/2} Pr^{1/3}
$$

$$
Sh = 2.0 + 0.6 \cdot Re^{1/2} Sc^{1/3}
$$

Boundary Conditions and Flame Layer

Symmetry boundary conditions apply at the center of the particle (all gradients are assumed to be zero). The model has two options for the boundary conditions at the particle edge. The first option is to use standard heat- and mass-transfer correlations to calculate the Nusselt and Sherwood numbers, as shown in Equations (12) & (13), to calculate the mass and heat transfer coefficients to the surface [51]. This option is best for pyrolysis calculations because it reduces calculation time. The second option is to extend the calculation domain past the solid surface into the gas phase. This gas-phase portion is described by a stagnant-film model. At the edge of the film, the conditions are considered to be the same as the bulk conditions in the reactor.

This second option is better for combustion modeling because it solves the transport equations in the region immediately surrounding the particle, or the boundary layer, thus resolving the gas properties near the particle surface, including the flame that often located there. Unlike small-particle (pulverized-coal, for example) combustion, reactions in particle boundary layer commonly occur during black liquor combustion. The boundary layer thickness is approximately proportional to the particle diameter and black liquor and many biomass particles are large enough that flames occur in the boundary layer and provide thermal feedback to the particles. Specifically, during devolatilization and char burning, significant amounts of combustibles evolve from the particle. If the boundary layer is very thin (relative to the reaction distance of the gas-phase components), these species simply diffuse from the surface and burn in the bulk gas. However, when the boundary layer is thick, these species burn within the boundary layer, thus reducing the oxidizer concentrations at the surface. When a flame is present during char burning, the combustion products, such as CO$_2$ and H$_2$O, diffuse back to the surface to gasify the char.

The gas flow around a sphere is really at least 2-dimensional, as is shown in Figure 17. This figure shows theoretical calculations using Fluent™ that describe typical fluid mechanics of a sphere entrained in a gas with a different velocity. On the upwind side of the sphere there is a stagnation point. On the sides of the sphere, there is a more fully developed boundary layer, and on the downwind side of the sphere, there is a recirculation
zone. This flow pattern creates non-uniform heat and mass transfer around the sphere. However, with a two-dimensional model (assuming the flow is axisymmetric around the particle), the flame zone surrounding the particle could be described by simply setting the boundary conditions at an arbitrarily long distance from the particle and solving the transport equations.

For a one-dimensional model, the flame zone surrounding the particle does not lend itself to precise modeling because flow in only one direction can be considered. In this approach, a film boundary layer is used. For a one-dimensional model in spherical coordinates, the radial direction, $r$, does not capture the effect of bulk airflow around the particle except by changing the film thickness, which is the distance from the particle surface to the bulk conditions [51]. With the bulk conditions set at an arbitrarily long distance from the particle (i.e. very thick film), a one-dimensional model can only accurately predict the boundary layer characteristics when the bulk gas is stagnant. However, by placing the bulk conditions closer to the particle, the heat and mass transfer rates accurately describe overall particle conditions even if axial/vertical flow and variations in the second dimension are ignored. The crucial variable is the film thickness. By increasing this distance, the temperature and species gradients decrease, and thus heat and mass transfer decrease.

Instead of describing the heat and mass transfer at each point on the particle surface, a 1-D model can only describe the average heat and mass transfer. The $Nu$ and $Sh$ correlations, shown above, work well for describing the average heat and mass transfer in a non-reacting boundary layer. The method developed for predicting the film thickness utilizes the accuracy of these correlations.

Estimating the film thickness, involves several assumptions. The first assumption is that standard heat and mass transfer correlations in conjunction with the stagnant-film model accurately describe mass and heat transfer and hence can be used to predict the film thickness [51]. Associated with this assumption are assumptions of a quasi-steady-state process, no angular flow (only radial flow) in the film, and no gas production sources in the film. The definition of the overall mass-transfer coefficient to a particle appears in Equation (14).

$$\theta_m$$ is the correction factor for advection from the particle, sometimes called the blowing factor, and the subscripts $O$ and $L$ represent the conditions at the surface and in the bulk, respectively. Because of these assumptions, the concentration profile for inert species in the film obtains from the steady-state advection-diffusion equation. Another as-
The derivative of Equation (15) yields an expression for the concentration/density gradient at the particle surface, \( \frac{dY_i}{dr} \). By substituting this expression for \( \frac{dY_i}{dr} \) into Equation (14) and solving for \( r_L \), the thickness of the film can be calculated. For very low bulk velocities, this calculation yields very large quantities for the film thickness. However, in the code, the film thickness is limited to ten times the particle diameter.

This equation has a singularity when the velocity equals zero. However, by applying L’hopital’s rule or by re-deriving this equation and ignoring the advection term, this problem can be eliminated. The result of the film thickness for low velocities is given in Equation (18).

The film thickness calculated from Equations (16) and (17) is only valid for mass transfer problems, and a different film thickness must be calculated for heat transfer. The derivation for the heat transfer film thickness is analogous to the derivation for the mass transfer film thickness. The additional assumptions are that the heat capacity and the thermal conductivity, \( \lambda \), in the film are taken to be the average heat capacity and the average thermal conductivity, respectively.

The most impressive results from using this method for calculating the film thickness are that it preserves the analytical solution for non-reacting, steady-state advection-diffusion problems, and that the effects of the flame inside the boundary layer can be predicted from the model. After implementing this method for determining the film thickness into the particle model, this method...
was tested to determine how well it worked for a particle during pyrolysis. Because there are no significant gas-phase reactions in the boundary layer during pyrolysis, the droplet model predictions based the method described above should be very similar to model predictions based on heat and mass transfer correlations during the transient and should converge to the same steady-state temperature at the end. The following figure shows the predicted particle surface temperature when each of the methods are employed in the droplet model. The predictions show that by specifying the thermal and mass transfer film thicknesses in the manner described above, the model still accurately predicts heat and mass transfer for the simple case of pyrolysis.

**Swelling and Drying Models**

Black liquor droplets swell to between 3-5 times their original diameter during devolatilization, which is one of its unique characteristics among low-grade fuels. The large impact this has on the structure may be more apparent when considering the implication for particle density for a nominally spherical particle. An increase in size by a factor of 5 coupled with a decrease in mass through devolatilization by, say, a factor of 2 implies a change in particle density by a factor of 250. To account for swelling, a swelling submodel makes the shell volume a function of the evaporation of moisture, devolatilization conversion, and char conversion. Each shell volume swells or shrinks independently of the rest. This model does not consider the droplet to be necessarily more porous near the center as some authors contend is the case [53]. Eq. (20) summarizes the overall swelling model. This model is based on that of Järvinen [53]. This investigation modified it to include shrinking during char burnout.

![Figure 18](image_url)

*Figure 18, Comparison of Stagnant Film Model with Standard Correlations Model for a 2-mm Droplet Pyrolyzing in 800°C Nitrogen.*
The variable `char_consumed` is the integral of the rate of char consumption with respect to time, and `char_produced` is the integral of the rate of char production with respect to time. The ratio of these numbers approaches unity from below, but not necessarily monotonically, as conversion increases. The $\beta$'s can be considered to be the ratios of the volume to the initial volume for drying, devolatilization, and smelt oxidation.

In this submodel, swelling during drying is instantaneous. Hupa et al. [54] showed that swelling during drying is initially very fast, but then practically stops for the rest of drying. Instantaneous swelling during drying may reasonably approximate the real behavior. The model assumes that there is a zero initial concentration of char in the particle. Some basis for determining shrinking during char consumption is required. This model uses the total char production as that basis. By using the total char production as the basis, as opposed to the char concentration during the previous time step, the shrinking model is more linear with char conversion. However, due to overlap between devolatilization and char burning, the particle starts shrinking before it finishes swelling; thus, the degree of swelling specified by the $\beta_B$ will not occur. Matching swelling with experimental data requires iteration with $\beta_B$.

The drying model uses a modified Raoult’s Law approach, modified because it is difficult to define mole fractions of black liquor. Boiling point data [26] provided a basis for an effective mole fraction for the black liquor as a function of moisture content. The regressed equation is actually based on mass fraction (solids content). The regression (Figure 19) resulted in Equation (21) as an expression for water vapor pressure as a function of composition and temperature, which is used in traditional mass- and heat-transfer models for particles in the remainder of the code. In this equation, $P_{w}$ is the partial pressure of water, and $P_{w,S}$ is the vapor pressure.

\[
P_{w,S} = 0.0716 \times (1 - Y_S)^{0.609} \times P_{w,S}^{sat}
\]  

(21)

**Pyrolysis Model**

The pyrolysis material in black liquor solids (B) devolatilizes into light gases, tar (T), and char (C). The tar converts into either light gas or char. Although this process is conceptually accurate, it does not preserve elemental conservation. Char in this model has the properties of graphite. The light gases are assumed to be a mixture of 1.9% H₂, 39.6% CO, 20.9% CO₂, 24.9% H₂O, and 12.7% light hydrocarbons. Thermodynamic properties of tar describe tar.

Because no devolatilization kinetics parameters were available for black liquor with the proposed mechanism, parameters were regressed from available literature data. A zero dimensional model was made of a single black liquor droplet, modified because it is difficult to define mole fractions of black liquor. Boiling point data [26] provided a basis for an effective mole fraction for the black liquor as a function of moisture content. The regressed equation is actually based on mass fraction (solids content). The regression (Figure 19) resulted in Equation (21) as an expression for water vapor pressure as a function of composition and temperature, which is used in traditional mass- and heat-transfer models for particles in the remainder of the code. In this equation, $P_{w}$ is the partial pressure of water, and $P_{w,S}$ is the vapor pressure.
during pyrolysis along with a code that performs nonlinear least squares using the Gauss-Newton method. Pyrolysis data from Iisa and coworkers [42] provided benchmark kinetic information. Least-squares analyses with this model provided parameter values. The resulting model predictions appear with the data in Figure 20.

Char Regeneration

The diffusivity model accounts for the porosity, \( \varepsilon \), and the tortuosity, \( \tau \); the latter is assumed to be 1.5, Equation (22). Near the end of char burning, the smelt becomes molten. The molten smelt’s porosity approaches zero and has a diffusivity orders of magnitude lower than the gas diffusivity. However, because the smelt agglomerates into beads, the underlying char structure is continuously exposed to the surrounding gases. To account for this mechanism, mass from the neighboring cell is added to the outermost cell during char oxidation. When 80% of the char has been consumed from the outermost cell, small amounts of adjacent cell are added to it to maintain the 80% char consumption until 99.9% of the particle is contained within the outermost shell. This rate of cell combination is consistent with Järvinen’s conclusions [34].

Thermodynamics and Kinetics

Table 6, Black Liquor Initial Composition.

<table>
<thead>
<tr>
<th>Species</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>68.78</td>
</tr>
<tr>
<td>Na(_2)S</td>
<td>0.00</td>
</tr>
<tr>
<td>K(_2)S</td>
<td>0.00</td>
</tr>
<tr>
<td>Na(_2)SO(_4)</td>
<td>1.38</td>
</tr>
<tr>
<td>K(_2)SO(_4)</td>
<td>0.10</td>
</tr>
<tr>
<td>Na(_2)CO(_3)</td>
<td>27.30</td>
</tr>
<tr>
<td>K(_2)CO(_3)</td>
<td>2.10</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.31</td>
</tr>
<tr>
<td>KCl</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The model attempts to make all of the thermodynamics completely consistent, meaning that each species includes thermodynamically consistent heat of formation and heat capacity values. En-
Table 5, Heat Capacities and Heats of Formation.

<table>
<thead>
<tr>
<th>Species</th>
<th>( C_p (\text{J}\cdot\text{kg}^{-1} \cdot \text{K}^{-1}) )</th>
<th>( \Delta H_f (\text{J/mol}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>[ \frac{1000 \cdot R_s}{7.72} \left( \frac{\exp\left(\frac{380}{T}\right)}{1800 \exp\left(\frac{380}{T}\right) - 1} + \frac{2 \exp\left(\frac{1800}{T}\right)}{1800 \exp\left(\frac{1800}{T}\right) - 1}\right) ]</td>
<td>-2.88E5*</td>
</tr>
<tr>
<td>C</td>
<td>[ \frac{1000 \cdot R_s}{11.3} \left( \frac{\exp\left(\frac{380}{T}\right)}{1800 \exp\left(\frac{380}{T}\right) - 1} + \frac{2 \exp\left(\frac{1800}{T}\right)}{1800 \exp\left(\frac{1800}{T}\right) - 1}\right) ]</td>
<td>1.317E6**</td>
</tr>
<tr>
<td>Tar</td>
<td>Same as benzene on a mass basis</td>
<td>4.20E4</td>
</tr>
</tbody>
</table>

*Based on an average heat of devolatilization between 500-800K of -80 kJ/kg [3]. **Based on Bryden’s measurement of heats of char oxidation [30]. ***Based on \( \Delta H_{\text{en,298k}} \) for Tar → Char where char is pure graphite [50]. Otherwise, coefficients come from [51].

Thalpys of pure species come from heat capacity and heats of formation information in the Gordon-McBride Thermodynamics Database [42]. Tar, in this model, has the specific heat capacity of benzene. The heat capacities and heats of formation of char (C), black liquor solids (B), and tar (T) appear in Table 5. All of the heats of reaction come from species enthalpies. All phases (gases and mixture) form ideal solutions. Initial species compositions come from softwood liquor data given by Järvinen et al. [53] as shown in Table 6.

For simplicity, the condensed-phase species enthalpies varied continuously as functions of temperature. Figure 21 shows an example of the resulting enthalpy as a function of temperature for sodium carbonate. This approach ignores solid-solid and solid-liquid phase transitions.

All reaction kinetics (other than pyrolysis reactions) for the model come from literature. Table 7 shows the kinetics and their respective references. In this table, species concentration, \( C_i \), has units of mol/m^3; \( MW_i \) is in kg/mol; \( r_i \) is in kg/m^3; and all rate expressions are in units of kg (of the first reactant)/m^3’s.

**Sodium Carbonate Equilibrium Model**

In their original investigation of sodium carbonate decomposition, Li and Van Heiningen found that carbon dioxide and carbon monoxide stabilize sodium carbonate. Published kinetics for the reverse reaction have not appeared since. To account for the stabilization of sodium carbonate by carbon monoxide and carbon dioxide, the model modified the original rate expression to be Equation (23).

\[
-r_{\text{Na}_2\text{CO}_3} = k_{18} \left( C_{\text{Na}_2\text{CO}_3} - C_{\text{Na}_2\text{CO}_3}^{\text{eq}} \right)
\]  

(23)

where the last term represents the equilibrium value of sodium carbonate at the current temperature and pressure. This expression prohibits the formation/desttruction of sodium carbonate from proceeding beyond its equilibrium point.

The equilibrium concentration of sodium carbonate was calculated two different ways. The first utilized HSC Chemistry 5.11® software, where \( N_2, \text{Na} (v), \text{Na} (l), \text{C} (\text{pure carbon}), \text{CO}, \text{and CO}_2 \)
Figure 21. Estimated Enthalpy of Sodium Carbonate.

Table 7. Chemical kinetics.

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Rate Expression (all units kg, mol, m, s, K)</th>
<th>E_i</th>
<th>A</th>
<th>n</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>B → light gas</td>
<td>$k_i(T) \cdot \rho_B$</td>
<td>6.40E7</td>
<td>1.4E5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>B → Tar</td>
<td>$k_i(T) \cdot \rho_B$</td>
<td>9.85E7</td>
<td>1.33E5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>B → Char</td>
<td>$k_3(T) \cdot \rho_B$</td>
<td>1.39E7</td>
<td>1.16E5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Tar → light gas</td>
<td>$k_i(T) \cdot \rho_g \cdot Y_T$</td>
<td>4.28E6</td>
<td>1.08E5</td>
<td>0</td>
<td>[52]</td>
</tr>
<tr>
<td>5</td>
<td>Tar → Char</td>
<td>$k_5(T) \cdot \rho_g \cdot Y_T$</td>
<td>1.00E5</td>
<td>1.08E5</td>
<td>0</td>
<td>[53]</td>
</tr>
<tr>
<td>6</td>
<td>Water evaporation</td>
<td>$SA_{M,H,i} \cdot h_{m,r} \cdot \rho_{H_2O} \cdot \rho_{H_2O,in} \cdot \frac{P_{H_2O} \cdot M_{H_2O}}{R_g \cdot T} \cdot \left(\rho_g \cdot Y_{H_2O}\right)$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[54]</td>
</tr>
<tr>
<td>7</td>
<td>Bound water evaporation</td>
<td>$k_7(T) \cdot \rho_{BM}$</td>
<td>5.13E10</td>
<td>8.80E4</td>
<td>0</td>
<td>[55]</td>
</tr>
<tr>
<td></td>
<td>Reaction</td>
<td>Rate Expression</td>
<td>Preexponential</td>
<td>Activation Energy</td>
<td>Reaction Order</td>
<td>References</td>
</tr>
<tr>
<td>---</td>
<td>-------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------</td>
<td>----------------</td>
<td>------------------</td>
<td>----------------</td>
<td>------------</td>
</tr>
<tr>
<td>8</td>
<td>( \frac{1}{2}O_2 + C \rightarrow CO )</td>
<td>( R_{\text{SA,C}} \cdot SA_{\text{C,V}} \cdot k_4(T) \cdot \rho_{\text{O}_2} )</td>
<td>0.658</td>
<td>7.48E5</td>
<td>1</td>
<td>[56]</td>
</tr>
<tr>
<td>9</td>
<td>( C + CO_2 \rightarrow 2CO )</td>
<td>( SA_{\text{C,m}} \cdot k_9(T) \cdot \rho_{C} \cdot C_{\text{CO}<em>2} / [C</em>{\text{CO}<em>2} + 3.4C</em>{\text{CO}}] )</td>
<td>3.92E5</td>
<td>2.50E5</td>
<td>1</td>
<td>[29, 57]</td>
</tr>
<tr>
<td>10</td>
<td>( C + H_2O \rightarrow CO + H_2 )</td>
<td>( SA_{\text{C,m}} \cdot k_{10}(T) \cdot \rho_{C} \cdot C_{\text{H}<em>2O} / [C</em>{\text{H}<em>2O} + 1.42C</em>{\text{H}_2}] )</td>
<td>1.60E4</td>
<td>2.10E5</td>
<td>1</td>
<td>[58]</td>
</tr>
<tr>
<td>11</td>
<td>( \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 )</td>
<td>( k_{11} \cdot \rho_{g} \cdot Y^0_{\text{CO}} \cdot C_{\text{O}<em>2} \cdot 0.25C</em>{\text{H}_2O}^{0.5} )</td>
<td>3.98E8</td>
<td>1.67E5</td>
<td>0</td>
<td>[59]</td>
</tr>
<tr>
<td>12</td>
<td>( \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} )</td>
<td>( k_{12} \cdot \rho_{g} \cdot Y^0_{\text{H}<em>2} \cdot C</em>{\text{O}_2}^{1.42} )</td>
<td>2.28E8</td>
<td>1.71E5</td>
<td>0</td>
<td>[60]</td>
</tr>
<tr>
<td>13</td>
<td>( C_6H_{6.2}O_{0.2} + 2.9O_2 \rightarrow 6.0CO + 3.1H_2 )</td>
<td>( k_{13} \cdot C_{T}^{0.5} \cdot C_{\text{O}<em>2}^{0.25} \cdot P^{0.3} \cdot MW</em>{T} )</td>
<td>20892</td>
<td>80235</td>
<td>1</td>
<td>[60]</td>
</tr>
<tr>
<td>14</td>
<td>( 2C + \text{Na}_2\text{SO}_4 \rightarrow \text{Na}_2\text{S} + 2CO_2 )</td>
<td>( k_{14} \left( \frac{C_{\text{Na}_2\text{SO}<em>4}}{C</em>{\text{Na}_2\text{SO}<em>4} + C</em>{\text{Na}<em>2\text{S}} + C</em>{\text{Na}_2\text{CO}<em>2}} \right)^{1.4} \cdot C</em>{\text{C,M}} )</td>
<td>3.79E3</td>
<td>7.81E5</td>
<td>0</td>
<td>[40]</td>
</tr>
<tr>
<td>15</td>
<td>( \text{K}_2\text{SO}_4 + 2C \rightarrow \text{K}_2\text{S} + 2CO_2 )</td>
<td>( k_{15} \left( \frac{C_{\text{K}_2\text{SO}<em>4}}{C</em>{\text{K}_2\text{SO}<em>4} + C</em>{\text{K}<em>2\text{S}} + C</em>{\text{K}_2\text{CO}<em>2}} \right)^{1.4} \cdot C</em>{\text{C,MW}} )</td>
<td>3.79E3</td>
<td>7.81E5</td>
<td>0</td>
<td>[40]</td>
</tr>
<tr>
<td>16</td>
<td>( \text{Na}_2\text{S} + 2O_2 \rightarrow \text{Na}_2\text{SO}_4 )</td>
<td>( k_{16} \cdot R_{\text{SA,Na}<em>2\text{S}} \cdot SA</em>{\text{C,V}} \cdot C_{\text{O}<em>2} \cdot MW</em>{\text{Na}_2\text{S}} )</td>
<td>6.23E5</td>
<td>7.81E5</td>
<td>0</td>
<td>[3]</td>
</tr>
<tr>
<td>17</td>
<td>( \text{K}_2\text{S} + 2O_2 \rightarrow \text{K}_2\text{SO}_4 )</td>
<td>( k_{17} \cdot R_{\text{SA,K}<em>2\text{S}} \cdot SA</em>{\text{C,V}} \cdot C_{\text{O}<em>2} \cdot MW</em>{\text{K}_2\text{S}} )</td>
<td>6.23E5</td>
<td>7.81E5</td>
<td>0</td>
<td>[3]</td>
</tr>
<tr>
<td>18</td>
<td>( \text{Na}_2\text{CO}_3 + 2C \rightarrow 2\text{Na} + 3\text{CO} )</td>
<td>( k_{18} \left( \rho_{\text{Na}_2\text{CO}<em>3} - \rho</em>{\text{Na}_2\text{CO}}^{\text{eq}} \right) )</td>
<td>1.00E9</td>
<td>2.44E5</td>
<td>0</td>
<td>[40]</td>
</tr>
<tr>
<td>19</td>
<td>( \text{K}_2\text{CO}_3 + 2C \rightarrow 2\text{K} + 3\text{CO} )</td>
<td>( k_{19} \cdot \rho_{\text{K}_2\text{CO}_3} )</td>
<td>1.00E9</td>
<td>2.44E5</td>
<td>0</td>
<td>[40]</td>
</tr>
</tbody>
</table>
Figure 22, Sodium Carbonate Equilibrium at 50 mol of Nitrogen per initial mol of Na$_2$CO$_3$.

were included in the equilibrium calculations. The second way simply uses Gibbs energy to calculate the equilibrium constant for the reaction shown in Equation (24), which we call the simplified approach. The simplified approach represents a scientifically rigorous approach, but it uses the same form of thermodynamic coefficients as is used in the rest of the model and it ignores the formation of a liquid phase. These two equilibrium calculations were compared and the Gibbs energy minimization equilibrium calculation was deemed adequate, and included in the model (see Figure 22 and Figure 23). The small differences arise from different thermodynamic coefficients used in the calculations.

**Model Limitations**

A one-dimensional droplet model has several limitations. As explained previously, the boundary layer surrounding the particle is non-uniform. Also, the particle temperatures and composition vary with angular and radial position. Commonly, a particle’s windward edges are hotter and burn out sooner than the leeward edges [13,16]. Additionally, non-uniformity in furnace conditions leads to non-uniform particle heating.
As shown in Figure 24 particle shapes are far from spherical [13,16] and the impact of the shape on conversion time and other properties can be dramatic. Capturing some of these complexities, such as the windward tendencies to burn out sooner and hotter than the leeward sides, lies within the grasp of multi-dimensional models, but others, such as the bizarre and rapidly changing shapes, depend on unknown and possibly stochastic processes that may prove very difficult to theoretically capture.

Modeling Results and Discussion
This section compares model predictions with the experimental data from the furnace and illustrates the effects of different assumptions on model predictions.

Comparison of Model Results with Experimental Data
This section discusses experimental data as compared to model predictions and problems associated with both.

Figure 25 compares predicted to measured temperatures, the latter measured by the thermocouple (internal) and the camera pyrometry (surface) techniques. The temperature is a good indicator of the dominate combustion stage as well as the extent of conversion of the droplet. In this case, the model accurately predicts the stages of combustion; the internal temperature measurement lies between the predicted center and surface temperature during drying and devolatilization and follows a similar trend to the measured temperature during char burning and smelt oxidation. If the end of smelt oxidation is taken to be the final bump in the temperature curves (between 13-14 seconds), the model and the measured overall conversion times agree within less than 4%.

The measured and predicted surface temperatures disagree substantially, especially in the early stages of combustion. As mentioned previously, the measured surface temperatures during particle heating are limited to regions of high temperature and are therefore biased toward high temperatures. Ip showed in his work that large temperature variations occur on the surface of the particle (about 400-500 °C during char burning and much higher for oxidizing vs non-oxidizing regions). The optical technique cannot record temperatures as low as the initial temperatures. The data suggest that, while the average particle surface temperature may be quite low initially, there are local regions of oxidation at very high temperatures that form

\[ \text{Na}_2\text{CO}_3 + C (\text{carbon}) \leftrightarrow 2\text{Na}_{(v)} + \text{CO}_2 + \text{CO} \]  \hspace{1cm} (24)
very early in the combustion process. This spatial variation in surface temperature, evident in the particle surface temperature images, cannot be captured by one-dimensional models.

One of the assumptions in the model is that the gas species in the particle are in thermal equilibrium with the surrounding particle. This assumption results in dramatic cooling of the char surface by the escaping pyrolysis gases. Because of the large pore size in black liquor char, it is possible that the path of escaping gas is not sufficiently tortuous to cause thermal equilibrium with the char. If the thermal equilibrium assumption were relaxed, it would increase the predicted temperature gradient and increase the predicted surface temperature. Additionally, a one-dimensional model necessarily assumes that gases uniformly exit the particle in all directions. The images clearly do not support such a conceptual mechanism. Apparently, there are regions of rapid particle outgassing and regions of relatively little outgassing, with significant differences in behavior on the particle surface.

Figure 26 illustrates measured and predicted droplet mass histories. Predicted and measured droplet mass follow the same trend, but exhibit about 0.3 seconds of offset. For this run, the droplet’s initial and final weights were 23.2 and 8.5 mg, respectively. The model predicted a final mass of 6.5 mg.
Figure 27 illustrates predicted and measured particle diameters. Although the model appears to over-predict swelling at the beginning of drying, the first point shown on the graph is the diameter of the droplet based on the droplets mass. As shown in previous investigations, the droplet begins swelling almost immediately. The maximum predicted diameter is higher than that measured, probably causing the predicted size decreases more rapidly than the measurements. Iterating on the swelling coefficient would correct the maximum size prediction. Droplet swelling behavior varies radically from sample to sample despite many efforts to homogenize the material and control conditions. Indeed, swelling produces highly aspherical particles with shapes that are difficult to capture with a single swelling parameter. Even though correlations indicate average swelling be-
Behaviors, there are large inherent stochastic variations in the swelling behavior among droplets.

**Effect of Typical Assumptions on Model Results**

Black liquor combustion involves extreme behaviors in many respects compared to other low-grade fuels. With typically 30% moisture, it contains similar moisture to other biomass fuels. It experiences extreme changes in size and density. With a typical volume increase of 35 times its original volume and an associated mass loss of 50%, the particle’s density decreases by up to two orders of magnitude between the initial value and the point of maximum swelling. The considerable swelling during periods of rapid heating contributes to large internal temperature gradients. The large quantity of inorganic species tends to increase the reactivity of black liquor very significantly, whereas in most fuels the ash can be assumed inert.

The following graphs show the effects of some modeling assumptions on black liquor combustion. The assumptions in this investigation include lumped capacitance (or an isothermal particle), no swelling, inert inorganic species, and no flame. This discussion examines each assumption sequentially to show its relative importance. Table 8 indicates the assumptions relating to each prediction for a 2-mm particle in 1073 K air. The swelling model assigned $\beta_B$ a value of 22. The first prediction has the most simplifying assumptions and is the simplest model, and the last prediction has the fewest assumptions and is the most sophisticated and accurate.

**Table 8. Modeling Assumptions Included in Prediction.**

<table>
<thead>
<tr>
<th>Assumptions</th>
<th>Prediction Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Flame</td>
<td>Y N N N N</td>
</tr>
<tr>
<td>No Swelling</td>
<td>Y Y N N N</td>
</tr>
<tr>
<td>Isothermal</td>
<td>Y Y Y N N</td>
</tr>
<tr>
<td>Inert Ash</td>
<td>Y Y Y Y N</td>
</tr>
</tbody>
</table>

Figure 28 shows the predicted droplet surface temperature during burning under different assumptions. Prediction 1 has the slowest overall conversion time. Prediction 2 shows the effect of a flame on the particle. The flame increases the surface temperature during devolatilization by 70 °C.

![Figure 28, Surface Temperature Predictions of a 2-mm Droplet in 750 °C Air and 0.2% Water Vapor, Gas Velocity .30 m/s.](image-url)
The overall conversion time is almost identical for the first two predictions, Figure 29 shows that the flame accelerates devolatilization and decelerates char burning, leading to largely offsetting influence on overall particle conversion time. During devolatilization, a flame forms inside the boundary layer, producing higher particle heat fluxes, thus accelerating devolatilization. During char burning, partial oxidation of carbon monoxide consumes some of the oxygen that would otherwise react at the surface. Because char gasification with carbon dioxide and water is slower than oxidation with oxygen, char burning decelerates. Prediction 3 shows the effect of swelling on the particle’s reactivity. Swelling decreases conversion time by half (from 11.5 s down to 5.5 s). Of all of the modeling assumptions, swelling has the most dramatic effect on the conversion time. Prediction 4 shows the effect of the isothermal assumption. Internal temperature gradients tend to increase the estimated conversion time, in this case by about 0.5 seconds.

Figure 29. Predicted Fractional Mass Loss of 2-mm Droplet in 750 ºC, Air and 2% Water Vapor, Gas Velocity .30 m/s.

Figure 30. Fraction Carbon and Water Remaining in a 17.3 mg Droplet of Black Liquor D in Air at 750 ºC, Gas Velocity = 0 m/s, Solids=70%.
Prediction 5 shows the impact of the inorganic chemistry. The inorganic species reactions increase particle temperature during char burning. The inorganic species reactions also increase the overall conversion time. This increase in conversion time is somewhat counterintuitive considering it involves including additional char consuming reactions. It occurs for two reasons. First, the inorganic species decrease the particle size during char conversion. During the early part of char conversion, sulfate reacts with char to produce CO₂ and sulfide. This char conversion decreases droplet size, thus decreasing total mass transfer (though increasing mass flux). Second, the sulfate/sulfide cycle is less efficient in its oxygen use than is direct oxidation of char with O₂. Although the sulfate donates all of its oxygen to char, the product of this reaction is CO₂, which is much less reactive than O₂, and much of the carbon leaves the droplet as CO₂. In the case of direct oxidation of char with O₂, much of the carbon leaves the particle as CO.

Prediction 5 indicates a large temperature spike due to the sulfide oxidation. After char conversion, the particle cools slower for prediction 5 because of sulfide oxidation reactions that continue after char burning.

Comparison to MBMS Data
The molecular beam mass spectrometer sampled the off-gases from the burning particle. If the off-gas sample is a representative sample, then the water peak should indicate the relative water evaporation rate plus the hydrogen oxidation rate. In addition, if one assumes complete combustion, the carbon dioxide concentration indicates the rate of carbon loss. Integration of these peaks over time yields the fractional water loss and carbon loss from the droplet.

Figure 30 illustrates carbon and water fractions remaining in an initially 17.3 mg (nominally 2 mm) droplet as measured by the MBMS compared to those predicted by the model. Obvious discrepancies appear between the measurements and the model predictions. Two major differences exist; (1) There is a time shift between the model predictions and the measurements by approximately 5-6 seconds; (2) The slopes of the curves (rates of reaction) differ significantly. The first discrepancy arises from the residence time of gases in the reactor and sample train prior to entering the MBMS. The reaction rates implied by MBMS data also are much slower, by approximately a factor of 2, than those predicted and those measured by the mass balance. This could arise from gas mixing in the sampling train or from velocity profile/chromatographic influences on the gas composition as it flows through the line. The MBMS data uniquely provide gas composition data, whereas the mass-loss data do not. It is possible that there

![Figure 31: Predicted Major Inorganic Species for a 23.2 mg Droplet of Black Liquor A at 800 °C in Air, Gas velocity=0.37 m/s, 95% Solids.](image-url)
are complex mechanisms leading to species mass loss rates implied by the data, but the accuracy of the drying model when tested alone (based on mass balance mass loss) is high, indicating that the MBMS results are probably compromised.

**Sulfate/Sulfide Cycle**

The sulfate/sulfide reactions oxidize char. The model indicates this mechanism is the most significant mechanism for char conversion by an inorganic species. Figure 31 shows the model prediction of the major inorganic species and indicates that carbonate decomposition is minimal during combustion at the specified conditions. On the other hand, the sulfate decreases to approximately 23% of its initial mass and then re-oxidizes after char conversion is complete. Sulfate oxidation converts one-sixth of the char to carbon dioxide.

**Conclusions**

This section summarizes the general conclusions to the document, including results derived from the both the experimental and the modeling results.

Experimental data from a novel single droplet reactor include simultaneous and temporal data on internal temperature, spatially resolved surface temperature, size, shape, images from multiple directions and mass data. These simultaneous data offer insight into black liquor reaction mechanisms and provide computer code verification and validation information. They are especially useful because of accurate furnace characterization (gas flow rates and furnace temperature). These mechanisms include, but are not limited to, particle drying, swelling, devolatilization, heatup, oxidation, and smelt formation.

Particle drying proceeds by a modified Raoult’s Law expression, where the mole fraction of water is replaced by a mass fraction expression. Mole fractions are difficult to define when dealing with black liquor and similar natural components. Model predictions agreed with measurements within their uncertainty limits.

New particle devolatilization parameters were regressed and validated. Devolatilization parameters yielded accurate amounts and rates of char and gas formation, as is further indicated from the prediction accuracy of char burnout times.

Char burnout time predictions and measurements are in good agreement. Most chars burn at or near diffusion limited rates; therefore these data provide little information on char burnout kinetics. They are representative of commercially significant char particle sizes and conditions.

An expression for the film thickness for a one-dimensional flame layer both predicts the presence of a flame and accounts for species steady-state heat/mass transfer in inert environments. This expression, suitable for a the type of transient and one-dimensional model developed in this document, does not account for the experimentally observed multidimensional flame structures around burning droplets/particles in suspension. Nevertheless, it appears to provide reasonably accurate estimates of flame affects on particle behavior.

Experimental evidence indicates that large internal temperature gradients, sometimes greater than 300 °C/mm, form during reaction, typically during drying/devolatilization. The model, however, does not always predict such large temperature gradients in the particle. This discrepancy possibly arises from the model assumption that the gas and the condensed phases are in thermal equilibrium. Because of the large pores, the path of escaping gases may not be sufficiently tortuous to cause thermal equilibrium. This assumption may lead to another model deficiency, that the maximum predicted surface temperature is consistently lower (never higher) than the measured surface temperature, by approximately 50-150 °C.

Sodium carbonate reactions with char proceed at negligible rates below 800 °C, largely due to equilibrium limitations. However, sodium sulfate reactions with char proceed under a broad range of temperatures and gas compositions and the sulfate/sulfide cycle is an important mechanism in char conversion (and smelt formation).

Smelt agglomeration during char burning exposes new char to the droplet surface. This mechanism minimizes the heat- and mass-transfer resistance to the char. To account for this mechanism in the model, neighbor nodes gradually donate mass to the outer cell, thus allowing char to be present in the surface cell throughout all of char burning. Predictions change significantly as modeling assumptions change. Swelling strongly influences overall reaction rates, decreasing overall conversion times by approximately 50% relative to predicted rates without swelling. Inorganic chemistry, internal temperature gradients, and the flame boundary layer also impact overall reaction rates by measurable amounts.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>Pixel area, m$^2$</td>
</tr>
<tr>
<td>$a_R$</td>
<td>Rosseland mean absorption coefficient, m$^{-1}$</td>
</tr>
<tr>
<td>$A_i$</td>
<td>Pre-exponential factor</td>
</tr>
<tr>
<td>$B$</td>
<td>Black liquor solids</td>
</tr>
<tr>
<td>$C$</td>
<td>Char</td>
</tr>
<tr>
<td>$c$</td>
<td>Concentration, mol·m$^3$</td>
</tr>
<tr>
<td>$char_{consumed}$</td>
<td>Mass of char consumed, kg</td>
</tr>
<tr>
<td>$char_{produced}$</td>
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<td>Pore diameter, m</td>
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<td>$D_{AB}$</td>
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</tr>
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<td>$D_{eff}$</td>
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<td>$f$</td>
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<td>Heat transfer coefficient, W·m$^{-2}$·K$^{-1}$</td>
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<td>Specific heats of reaction, J·kg$^{-1}$</td>
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<td>Binary diffusivity, m·s$^{-2}$</td>
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<td>$D_K$</td>
<td>Knudsen diffusivity, m·s$^{-2}$</td>
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<td>Prandtl number</td>
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<tr>
<td>$r$</td>
<td>Radius coordinate, m</td>
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</table>
Δr  Reaction rate, kg·m⁻³·s
Re  Film thickness, m
Re  Reynolds number
Rg  Universal gas constant, 8.3145 J·mol⁻¹·K⁻¹
Rp  Particle radius, m
RSA  Surface area ratio, RSA, f = ρ/ρtot
SG()  Spectral responsivity function
SA  Surface area
S  Source term
Sc  Source term linearization
Sh  Schmidt number
Sp  Sherwood number
Sp  Source term linearization parameter S = Sp·Tp + Sc
T  Time, s
T  Temperature, K
u  Gas velocity, m·s⁻¹
Y  Mass Fraction
hm  Mass transfer coefficient
fsp  Fiber saturation point
X  Magnification
Xi  Mole fraction
ν  Particle volume

Greek Symbols
α  Shrinking factor
β  Volume ratio
ε  Porosity
η  Permeability
λ  Wavelength, m

μ  Thermal conductivity, W·m⁻¹·K⁻¹
ρ  Viscosity, Pa·s
ρ  Density, kg·m⁻³
σ  Boltzmann constant, W·m⁻²·K⁻⁴
ω  Emissivity
η  Ratio of biomass to the initial black liquor
    solid (or biomass), char and ash
θ  Blowing factor
τ  Tortuosity

Lens transmission factor
<table>
<thead>
<tr>
<th>Subscripts</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Initial value or reference state</td>
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<tr>
<td>B</td>
<td>Biomass</td>
</tr>
<tr>
<td>Blue</td>
<td></td>
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<td>1, …, 21</td>
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<td>C</td>
<td>Char</td>
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<td>Combined</td>
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<td>Effective</td>
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<td>Gas phase</td>
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<td>Light gas</td>
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</tr>
<tr>
<td>I</td>
<td>Inert gas</td>
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<td>Solid species</td>
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<tr>
<td>ini</td>
<td>Initial</td>
</tr>
<tr>
<td>j</td>
<td>Gas species</td>
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<tr>
<td>k</td>
<td>Water species (bound and free)</td>
</tr>
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<td>L</td>
<td>far edge of boundary layer</td>
</tr>
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<td>m</td>
<td>Mass transfer</td>
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<tr>
<td>M</td>
<td>Moisture</td>
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<td>r</td>
<td>r-direction</td>
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<td>Red</td>
</tr>
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<td>rad</td>
<td>Radiation</td>
</tr>
<tr>
<td>S</td>
<td>Solid phase</td>
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<tr>
<td>T</td>
<td>Tar</td>
</tr>
<tr>
<td>Thermal</td>
<td></td>
</tr>
<tr>
<td>tot</td>
<td>Total condensed phase</td>
</tr>
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<td>TS</td>
<td>Time stamp</td>
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<tr>
<td>V</td>
<td>Water vapor</td>
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<td>w</td>
<td>West control volume surface</td>
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<table>
<thead>
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<th>Definition</th>
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<tr>
<td>sat</td>
<td>Vapor pressure</td>
</tr>
<tr>
<td>V</td>
<td>Water vapor</td>
</tr>
</tbody>
</table>
References


KINETICS OF KRAFT BLACK LIQUOR COMBUSTION

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SAINT PETERSBURG STATE TECHNOLOGICAL UNIVERSITY OF PLANT POLYMERS,
SAINT PETERSBURG, RUSSIA

Introduction

The study of kinetics of kraft liquor droplets combustion and development of a mathematical model for recovery boiler furnace processes meets considerable difficulties because of high temperatures, corrosive medium, and a variety of processes taking place at a furnace.

Combustion of black kraft liquor at modern recovery boiler furnaces is based on coupling of flame and fuel-bed combustion and consists of three major stages: evaporation, release of volatile organic combustibles, and coke carbon burning out. Different physical-chemical processes proceed also with mineral components of the liquor.

At the recovery boiler furnace, drying of a liquor droplet takes place at high heat transfer potential and significant intraparticle temperature gradient. Under these conditions, the first drying period (the period of constant drying rate) when moisture content on the particle surface approaches to its critical value and surface temperature is constant and equal to a wet-bulb temperature does not exist.

The period of decreasing drying rate when the rate is determined by that of water diffusion to the particle surface runs with evaporation surface deepening inward the particle.

Combustion and gasification kinetics of partly dried and inflamed liquor particles is rather complicated. The combustion of volatile substances arising from a liquor particle surface occurs with simultaneous oxidation of an outer coked layer and water release from an inner moist zone.

Investigating black liquor combustion

The experimental study of liquor drying and burning kinetics has been carried out at the Department of Industrial Heat-Power Engineering of the Saint Petersburg State Technological University of Plant Polymers [1]. Black kraft liquor sampled at the recovery boiler fuel guns of the Pitkäranta Pulp Mill has been studied. Its relative moisture content was no more than 40%.

For experiments with dry liquor particles, the moist liquor was dried for the final moisture content to be no more than 1%. Then the dry liquor was ground and screened by fractions 0.25, 0.5, 1.0, 1.25, 2.0, 3.0 mm. The study of moist liquor combustion was carried out with liquor particles of relative moisture content 25%. This moisture content value was obtained after drying the initial liquor at a dewatering box at 105°C. Spherical particles of diameter 1, 2, 3, 4, and 5 mm were produced from this liquor.

Initial chemical composition of liquor dry substances was practically unchanged during the research and is given below:

Organic components: $C^d = 38\%; O^d = 16.45\%; H^d = 4.25\%; N^d = 0.35\%; S^d = 1.9\%$

Mineral components: $NaOH^d = 17.9\%, Na_2CO_3^d = 6.04\%, Na_2S^d = 1.47\%, Na_2SO_4^d = 7.5\%, NaOH^d = 1.67\%$

Combustion of individual moist liquor particles has been investigated with an experimental device consisting of quartz tube 120 mm in inner diameter incorporated into an electric furnace. Liquor particles of diameter from 1 mm to 5 mm and moisture content 25% were fixed on junctions of platinum to platinum-rhodium thermocouples or on platinum electrode wires 0.2 mm in diameter.

The thermocouples with liquor particles and the tube were fastened to a carriage. For inserting the
carriage into the furnace rapidly, a special mechanism was used. After a preset period of time, the thermocouples or wires with the particles were withdrawn from the reactor into a chamber cooled with nitrogen flow.

The furnace temperature was automatically controlled and gas medium composition was sustained by operation of gas-fired injector burners. The experiments were conducted at gas (air) temperatures 1173 K, 1273 K, and 1373 K. Air or gas combustion products were supplied to the tube furnace at excess air coefficients 0.88, 1.0, 1.2, and 1.4.

**Results**

It follows from analysis of these experimental results that significant increase in sizes of burning particles occurs during their heating. For the particles of initial diameter 1 mm and 2 mm there was 50-fold increase in their volume and 30-40 times for the particles of initial diameter 3 mm to 5 mm. At the furnace temperature 900 oC, a period of particles drying and warming-up to ignition comprised 20% of the total process duration. During the whole combustion period, a particle is surrounded with flame. Before finishing the burning process, a drastic increase in temperature inside a particle and its breakdown happen, with the smallest sparks consisting of mineral salts leaving the particle. Based on the experimental results, average reduced rate constants of liquor burning have been calculated. They can be used as the basis for thermal calculations of recovery boiler furnaces.

The experimental residual moisture content of liquor droplets vs. period of their staying at the furnace at different temperatures is shown in Figure 1.

Temperature measurements in a droplet center with the use of a thermocouple at the furnace temperature T=1273 K show that warm-up and partial water evaporation takes place during four seconds for the particles of initial diameter 3 mm and during 6 seconds for the particles of initial diameter 4 mm, with the temperature in a droplet center being close to that of water evaporation.

Volatile substances ignite when the surface temperature is close to 513 K and the duration of total drying of the droplets far exceeds the actual time of particles warming-up to their ignition that comprises 25-30% of the total drying duration.

The droplet ignition takes place when dry layer width (δ) approximates 0.2 of the drop radius. Further processes of drying, volatiles release and their combustion go on simultaneously.

The time of total water evaporation from a droplet (τe) and the temperature of outer surface of a dry layer (τs) are recommended to be determined from the equations:

\[
\tau_e = \frac{\rho g \left( \frac{r_0^2}{6\lambda_d} + \frac{r_0^3}{3\alpha} \right)}{t_g - t_e}, \quad \text{sec},
\]

\[
t_s = t_g - \frac{t_g - t_e}{\alpha \cdot r_0^2 \left( \frac{1}{\lambda_d \cdot r_e} - \frac{1}{\lambda_d \cdot r_0} + \frac{1}{\alpha \cdot r_0^2} \right)}, \quad ^\circ\text{C},
\]

Figure 1, Residual moisture content (W,%) of liquor droplets vs. time at the furnace for different furnace temperatures (droplet diameter: 1 - 2 mm; 2 - 3 mm; 3 - 4 mm; 4 - 5 mm).
where $q$ is the heat of warm-up and water evaporation; $\rho$ is the density of material; $t_g$ and $t_e$ are respectively the gas flow temperature and the temperature on the evaporation surface of radius $r_e$; $r_o$ – an initial radius of a particle; $\lambda_d$ – the thermal conductance of a dry particle; $\alpha$ is a coefficient of heat transfer on particle surface, $t_s$ is the temperature of liquor droplet surface.

The plots obtained with these equations (Figure 2) are in good agreement with experimental data.

**Black liquor pyrolysis**

While studying pyrogenic decomposition of kraft liquor, the procedure based on regular weight recording for the samples heat treated in pure nitrogen flow was applied. Liquor weighed portions were being kept at temperatures 423 K, 473 K, 573 K, 673 K, 773 K, 873 K, 1073 K, and 1173 K up to complete release of volatile substances (Figure 3). Char residue level was also determined together with measuring volatile-matter yield.

Volatile release started at 423 K. The amount of volatiles released depends on temperature. At the temperature 1073 K, their yield comprises 67%, at 673 K – 20%, and at 473 K – 13% providing the time of weighed portions calcination was the same.

The study of pyrogenic decomposition of kraft liquor in an inert medium at the temperatures ranging from 423 K to 1173 K has demonstrated that thermal decomposition of the liquor started at 423 K – 433 K. Volatiles release increases as temperature increases and at the temperatures 973 K and higher losses of mineral components take place. At the temperature 523K, maximum velocity of black liquor volatiles release has been observed.

**Organics burn-out**

Experimental study of liquor organics burn-out has shown that burn-out velocity depends on the furnace temperature. The burn-out velocity increased 1.7 times for particles of the same diameter as the furnace temperature increased from 1173 K to 1323 K. Initial size of the particles affected also
the velocity of organic matter burn-out. The velocity decreased with increasing initial size of the particles. For example, the burn-out velocity differed almost two times for the liquor particles of diameter 1 mm and 3 mm. Figure 4 demonstrates some results of these experiments.

From chemical analysis of mineral components of both dried liquor weighed portions and individual moist particles it follows that their conversions are similar. When introducing weighed portions of dried liquor into furnace, chemical reactions are characterized by higher rates than those taking place in moist liquor combustion.

Chemical analysis of mineral components of moist liquor particles partly burnt-out at different period of heat treatment shows the unchanged sodium sulfide level under given heat treatment conditions. Sodium sulfate level slightly decreases as compared to the initial one and sodium carbonate content increases markedly. Alkali carbonization begins immediately with introduction of the studied weighed portion into the furnace.

Based on the results obtained the conclusion was drawn that at rapid burn-out of suspended liquor particles in the oxidative medium sodium sulfate was hardly reduced to sulfide. Carbonization of liquor was a dominant process. Sodium hydroxide (including organically bonded one), sodium sulfide as well as salts of different organic acids take part in chemical reactions resulted in formation of sodium carbonate and sodium sulfate. As a result of sodium sulfide carbonization, a part of carbon dioxide was converted into sodium carbonate.

**Figure 3.** Volatiles release (Vd) vs. time at the furnace and furnace temperature.

**Figure 4.** Changes in sodium carbonate level and velocity of liquor organics burn-out (b, %) for the particles of diameter 3 mm and 4 mm at the temperature 1273 K and air excess $\alpha = 0.88; 1.0$. 
ate to yield hydrogen sulfide which while burning down gave water and gaseous sulfur dioxide.

Sodium carbonate level at the liquor weighed portions increased drastically more than three times in an initial period of heat treatment peaking at the time equal to 0.4 – 0.5 of the total combustion period. Then the sodium carbonate level decreased because sodium carbonate reduction and evaporation became prevailing over reactions of sodium carbonate formation.

Chemical analysis of the smelt obtained in the course of experiments has shown that sodium sulfate was partially reduced only at a final stage of the process. In this case, Na₂S and Na₂SO₄ levels in the smelt were found to comprise respectively 2.7 % - 9.3% and 2.6 % - 10.6 %. The reduction value of sodium sulfate increased with increasing temperature and initial size of liquor particles. The maximum Na₂S level (9.29%) has been found out in combustion of moist liquor particles of initial diameter 5 mm at α = 1 and the furnace temperature 1273 K.

**Terminal velocity**

Because of significant changes in sizes and forms of liquor particles in the course of their combustion it is difficult to calculate terminal velocity for the burning particles. At the same time, the terminal velocity is an important parameter of liquor particles combustion. That is why the experiments have been conducted to determine the terminal velocity for particles of different diameters at varying air excess and temperature.

It has been determined that the terminal velocity changed in a similar manner for particles of all diameters and under all conditions investigated. The minimum velocity value was in the range from 0.9 m/sec. to 1.2 m/sec. for the particles of diameter 1mm – 5 mm, with the initial terminal velocity ranging from 11 m/sec. to 12 m/sec. for original particles. The minimum value of terminal velocity was achieved at relative burning time 0.6 – 0.7.

Analysis of the results obtained has shown that the lesser is the diameter of a burning particle and the higher are air excess and furnace temperature, the faster is the decrease in the terminal velocity up to its minimum value.

Changes in the terminal velocity of liquor droplets depending on the burning time at the coefficient of air excess α = 1 and the temperature 1373 K are shown in Figure 5 (diameter of droplets: 1 – 1 mm; 2 – 2 mm; 3 – 3 mm; 4 – 4 mm; 5 – 5 mm).

**New air arrangement**

A large set of experiments aimed at studying kinetics of liquor combustion, physical-chemical processes in smelt and aerodynamics of kraft liquor particles has made it possible to work out a procedure for calculating burn-out parameters and liquor droplets paths at a recovery boiler furnace [2] as well as to develop and introduce a radically

---

**Figure 5. Changes in the terminal velocity (Wh) of liquor droplets.**
new scheme of liquor combustion in intercrossing jets [3].

The method proposed is based on a radically new aerodynamic scheme of liquor combustion in intercrossing jets under U-shaped flame motion. The project has been implemented at the Kotlas Pulp & Paper Mill where the “Tampella” recovery boiler has been upgraded through arranging aerodynamic pinch formed with front and rear water-wall tubes at the secondary air level. The secondary air was introduced into a furnace with 20 adjustable nozzles (positioned on two noses of ten each), with air jets being directed at the angle 60° to the furnace bottom. Liquor guns are located on the front and rear walls below the level of secondary air nozzles by 0.9 m. Tertiary air was completely removed, primary air was unchanged.

Secondary air produces a continuous flat jet at the level of liquor guns. Injecting action of this jet causes inflow of liquor combustion products to air jet root initiating vortex motion. Air jets intersect liquor ones, entrain small-sized liquor droplets (which don’t require long preparation to their ignition) in the bottomward direction. Large-sized droplets are in inertial motion to a central furnace zone and then fall slowly downwards by gravity in gas upflow.

Thus, in accordance with dispersivity of liquor droplets, their separation as well as adjustment of duration of their stay at the furnace takes place in these intersecting jets.

Air supply is directed to a root of fuel jets providing conditions for rapid formation of a homogeneous fuel mixture and intensive preparation of fuel droplets to their ignition. Inflow of combustion products from the furnace due to injecting action of air jets contributes also to this process. In so doing, vortex motion of combustion products and fuel droplets arises in a vertical plane contributing also to intensifying the combustion process and complete burning-out of combustibles.

Operation of the system has demonstrated its efficiency including reduction in flue dust [4].

Figure 6, Vortex furnace of recovery boiler: 1 – furnace; 2 – liquor guns; 3 – secondary air; 4 – aerodynamic nose.
References
GETTING RID OF POTASSIUM AND CHLORIDE

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ANDRITZ OY
TAMMASAARENKATU 1
00180 HELSINKI

Introduction

Modern Kraft mill chemical liquor cycles are more and more closed, causing an accumulation and hence high concentration of Non Process Elements (NPE) in liquor streams which is harmful to the mill operation. High chloride and potassium content in black liquor increase the risk for corrosion and plugging in recovery boilers.

Chloride and potassium are enriched in electrostatic precipitator ash and therefore ESP ash is a favorable stream to process when aiming to control the chloride and potassium content of the whole Kraft liquor cycle. In the paper three different commercial chloride control methods are described and compared.

- Ash out take (dumping)
- Leaching
- Ash Crystallization

In all chloride removal methods also valuable ESP ash chemicals will be lost. Because main part of ESP ash consists of valuable process chemicals, sodium sulfate and sodium carbonate, the value of sodium losses has to be accounted for. The sodium losses depend in addition to the selected process and chloride input to the mill also on the required chloride + potassium removal, Cl + K concentration in the ash (or in black liquor). The performances of the three processes are presented as a function of required chloride removal rate and Cl-concentration in the ash.

Effect of chloride and potassium content on recovery boiler fouling

Composition of dust from recovery boiler furnace (ESP ash) varies much depending on liquor properties and firing conditions including the heat load and especially of the concentration of the potassium and chloride in the firing black liquor. In Table 1 is the range of major components in ESP ash presented.

<table>
<thead>
<tr>
<th>Component</th>
<th>wt-%</th>
<th>Compound</th>
<th>wt-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>28 - 35</td>
<td>Na₂SO₄</td>
<td>65 - 90</td>
</tr>
<tr>
<td>SO₄</td>
<td>45 - 65</td>
<td>Na₂CO₃</td>
<td>5 - 20</td>
</tr>
<tr>
<td>CO₃</td>
<td>5 - 15</td>
<td>NaCl</td>
<td>2 - 10</td>
</tr>
<tr>
<td>K</td>
<td>2 - 10</td>
<td>K₂SO₄, KCl</td>
<td>5 - 20</td>
</tr>
<tr>
<td>Cl</td>
<td>1 - 5</td>
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</table>
The tendency of ash to form deposits is related to the smelt behavior of the ash. Smelting curve depends on ash composition, generally a high chloride and potassium concentration causes low sticky temperature $T_{15}$, therefore high Cl+K requires, to avoid fouling and corrosion, low steam temperature to obtain low surface temperature for the superheater tubes.

Figure 1, Sticky temperature $T_{15}$ as function of chloride and potassium content in ESP ash; Point 1. Ash Cl-content = 8 mol-% (4 wt-%) and K = 9 mol-% (5 wt-%) $\Rightarrow$ $T_{15} = 580$ °C, Point 2. Cl = 2 mol-% (1 wt-%) and K = 3,6 mol-% (2 wt-%) $\Rightarrow$ $T_{15} = 700$ °C.

In practice some safety margin for the maximum allowed temperatures has to be reserved. Generally, the following maximum chloride and potassium concentrations (Table 2) are recommended:

To make detailed estimation for “safe, non-fouling” maximum chloride and potassium content, boiler CFD calculations including temperature profile and smelt curve for the ash have to be done.

Depending on construction materials risk for chlorine corrosion may be the limiting factor to maximum allowable temperature.

Table 2, Recommended maximum concentrations for Cl and K.

<table>
<thead>
<tr>
<th>Steam Temp. / C</th>
<th>Virgin BL Cl / %</th>
<th>Virgin BL K / %</th>
<th>ESP ash Cl / %</th>
<th>ESP ash K / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 480</td>
<td>0.5</td>
<td>1.5 - 3</td>
<td>2.5</td>
<td>4 - 7</td>
</tr>
<tr>
<td>&lt; 500</td>
<td>0.2 - 0.3</td>
<td>1 - 2</td>
<td>1 - 1.5</td>
<td>2.5 - 5</td>
</tr>
<tr>
<td>&gt; 500</td>
<td>0.15</td>
<td>1 - 2</td>
<td>1 - 1.5</td>
<td>2.5 - 5</td>
</tr>
</tbody>
</table>
Chloride and Potassium sources and losses in liquor cycle

The NPE input sources and losses in liquor cycle are listed in Table 3. Cl- and K-input from wood depends largely on the soil and transportation (e.g. sea floated). Flue gas losses are connected to SO2 emissions, the higher liquor DS the lower SO2 and Cl emissions, with DS over 75 % the losses are practically zero.

In euca mills typical net input for chloride is 1 – 3 kg Cl /ADT and for potassium 2 – 5 kg K / ADT and for the soft wood respectively 0,3 – 1 kg Cl /ADT, 1 – 2 kg K / ADT.

Chloride and potassium enrichment in ESP ash

Chlorides and potassium compounds have higher vapor pressures than sodium sulfate. This results in their preferential volatilization from the smelt bed into the ash stream. As a result, chloride and potassium have higher concentrations (of DS) in ash than in virgin black liquor.

The enrichment is usually defined as the ratio in the dust to the content in virgin black liquor. In the calculation the contents are expressed as the molar ratio of chloride and respectively of potassium to the sum of sodium and potassium, enrichment factors for Cl and K in equations 1 and 2. Concentrations in the equations are expressed as mol-%.

\[
E_{\text{Cl}} = \frac{[\text{Cl} / (\text{Na} + \text{K})]_{\text{ash}}}{[\text{Cl} / (\text{Na} + \text{K})]_{\text{virgin BL}}}
\]

\[
E_{\text{K}} = \frac{[\text{K} / (\text{Na} + \text{K})]_{\text{ash}}}{[\text{K} / (\text{Na} + \text{K})]_{\text{virgin BL}}}
\]

Cl and K enrichment factors vary very much (Table 4). This depends on liquor properties, potassium and chloride concentrations, firing conditions and especially on heat load.

Rough estimate for typical enrichment factors on weight basis for chloride = 5 and for potassium = 2.5. E.g. If Cl in virgin liquor = 0.5 wt-%, Cl in ash = 2.5 wt-%.

**Table 3, Chloride and potassium sources and losses.**

<table>
<thead>
<tr>
<th>Source</th>
<th>kg Cl / ADt</th>
<th>kg K / ADt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>0.2 – 3</td>
<td>0.4 – 3</td>
</tr>
<tr>
<td>Make up chemicals and water</td>
<td>0.2 – 0.8</td>
<td></td>
</tr>
<tr>
<td>Waste acid</td>
<td>0.1 – 0.5</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4, Enrichment factors.**

<table>
<thead>
<tr>
<th>NPE</th>
<th>Range mol/mol</th>
<th>Typical mol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>0.3 - 6</td>
<td>2.6</td>
</tr>
<tr>
<td>Potassium</td>
<td>1 - 2.5</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Chloride and potassium removal methods

Modern methods to control chloride and potassium content in ESP ash are:

- Ash out-take (dumping)
- Ash leaching
- Ash crystallization, Andritz Ash ReCrystal lization, ARC

Ash dumping is widely used in the industry, with no need or low investment costs but chemical losses are high. The two other methods are based on solubility differences between different ash components: chloride and potassium compounds are more soluble than sulfates and carbonate.

Ash leaching

In leaching process (Figure 2) ESP ash is mixed with hot water in ratios of 1 – 1.5 kg ash / kg water forming slurry: ash is only partially dissolved in water. Most of chloride and potassium compounds are dissolved in water while major part of sodium sulfate and carbonate remain as solids in the slurry. The slurry is pumped from the mixing tank to a decanter centrifuge that separates solids from liquid. The filter cake is returned to black liquor mix tank and the filtrate, enriched in chloride and potassium is purged to sewer.

When carbonate (CO₃) concentration in the ash is over 5 %, the settling velocity of the slurry particles becomes very low and the ash cake remains very wet, meaning that Cl and K removal rates are decreased and sodium losses are increased. The carbonate concentration can be decreased by adding sulfuric acid in the leaching tank, the pH is decreased from 10 - 11 to 9 – 9.5. The acid will react with carbonate forming sodium sulfate and carbon dioxide according to the formula below:

\[ \text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 \downarrow + \text{CO}_2 \uparrow + \text{H}_2\text{O} \]

The acid consumption depends on the carbonate content in the ash. For example: if the untreated ash contains 10 % carbonate about 80 kg sulfuric acid / ton of ash is required to decrease the carbonate concentration down to 5 %. The added acid is not wasted; it compensates partially the need of sodium sulfate make up to the liquor cycle.

![Figure 2, Principle of Ash Leaching.](image)

![Figure 3, Principle of Ash Crystallization.](image)
Ash crystallization, ARC
In crystallization process ESP ash is first dissolved completely in hot water (or condensate) in ratios of 0.3 – 0.6 kg ash / kg water. The solution is fed to evaporative crystallizer where most of sodium sulfate and carbonate is crystallized and most of chloride and potassium compounds remain in the solution. The crystal slurry is pumped from the crystallizer to the centrifuge where crystals and liquid are separated. The filter cake is returned to black liquor mix tank and the filtrate, enriched in chloride and potassium is purged to sewer.

Metal ions in the removal process
ESP ash water solution has pH 10 -11. Most metal ions form insoluble hydroxides in basic solutions and therefore metals in the ash are returned back to liquor cycle with centrifuged cake from the removal process and only 2 – 15 % is purged to the sewer or otherwise: 85 – 98 % of metals are recovered.

Comparison of chloride and potassium removal processes
Chloride and potassium removal efficiency depends on ash composition and is related to chemical losses in each controlling method, part of the process elements and compounds are purged with Cl and K to sewer. Typical chloride removal efficiency for leaching and crystallization processes is presented in figure 4 as a function of sodium losses.

Potassium removal efficiency is about the same as that for chloride when potassium content in the ash is less than 4 wt-%. In higher potassium concentration glaserite, K₃Na(SO₄)₂, co-crystallizes with sodium sulfate and potassium removal will be decreased remarkably. So when a Cl&K removal process is installed in an existing mill with high potassium content, ash has to be taken out as ESP dust until the potassium concentration in ESP ash has decreased to about 4 %.

Table 5, Measured metal concentrations in an ARC process.

<table>
<thead>
<tr>
<th></th>
<th>Virgin BL</th>
<th>Esp Ash</th>
<th>Crystals from ARC</th>
<th>Purge from ARC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>mg/kg ds.</td>
<td>&lt; 200</td>
<td>39.4</td>
<td>37.0</td>
</tr>
<tr>
<td>Cd</td>
<td>mg/kg ds.</td>
<td>&lt; 0.4</td>
<td>0.28</td>
<td>0.41</td>
</tr>
<tr>
<td>Co</td>
<td>mg/kg ds.</td>
<td>&lt; 2</td>
<td>0.15</td>
<td>0.26</td>
</tr>
<tr>
<td>Pb</td>
<td>mg/kg ds.</td>
<td>&lt; 4</td>
<td>9.94</td>
<td>17.4</td>
</tr>
<tr>
<td>Mg</td>
<td>mg/kg ds.</td>
<td>345</td>
<td>168</td>
<td>97.8</td>
</tr>
</tbody>
</table>

![Figure 4](image-url)
Figure 4 shows that the crystallization process is much more effective and has less chemical losses than the leaching process. Depending on the required chloride and potassium content in ash and the input of Cl and K into the liquor cycle, we will only need to treat a part of the ash in most cases, to reach an acceptable concentration for Cl+K. In such cases, the efficiency of the Cl + K removal process will, with respect to the chemical losses, have a less significant role to determine the process alternative that is most cost effective.

While each pulp mill has different ash composition Andritz has developed a comprehensive liquid-solid equilibrium program by which the two processes can be well simulated and the optimum process alternative for the specific case can be selected.

In Table 6 is the ash re-crystallization (ARC) and leaching processes compared with respect to the ash out-take.

Investment costs for ash out-take is much lower than the other removal processes in table 6, but the annual make up chemical costs are very high. Depending on mill sulfur and sodium balances the share of the make up chemicals may be different from the figures shown in the table. Generally the pay back time for the investment costs of ARC or leaching is less than one year compared to total out-take costs.

**Table 6, Comparison of Cl and K removal processes.**

<table>
<thead>
<tr>
<th>Mill data</th>
<th>ESP Ash Component</th>
<th>wt-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp production</td>
<td>ADt/d 2 000</td>
<td>Na</td>
</tr>
<tr>
<td>Recovery Boiler</td>
<td>ton DS/d 3 500</td>
<td>K</td>
</tr>
<tr>
<td>K removal</td>
<td>kg/ADt 1.1</td>
<td>Cl</td>
</tr>
<tr>
<td></td>
<td>ton/d 2.3</td>
<td>SO4</td>
</tr>
<tr>
<td>Cl removal</td>
<td>kg/ADt 0.4</td>
<td>CO3</td>
</tr>
<tr>
<td></td>
<td>ton/d 0.9</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process</th>
<th>ARC</th>
<th>Leaching</th>
<th>Out take</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESP ash feed</td>
<td>ton/d 108</td>
<td>111</td>
<td>87</td>
</tr>
<tr>
<td>of ash</td>
<td>% 39</td>
<td>40</td>
<td>31</td>
</tr>
</tbody>
</table>

**Removal (of treated ash)**

| K     | % 80 | 80 | 100 |
| Cl    | % 80 | 80 | 100 |

**Loss**

<table>
<thead>
<tr>
<th>Na (of treated ash)</th>
<th>% 20</th>
<th>30</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>ton/d</td>
<td>7</td>
<td>10</td>
<td>28</td>
</tr>
<tr>
<td>kg/ADt</td>
<td>3.5</td>
<td>5.2</td>
<td>14</td>
</tr>
<tr>
<td>SO4</td>
<td>ton/d 6</td>
<td>16</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>kg/ADt</td>
<td>2.9</td>
<td>8.1</td>
</tr>
</tbody>
</table>

**Make up chemicals (100%)**

<table>
<thead>
<tr>
<th>H2SO4</th>
<th>ton/d</th>
<th>8.6</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg/ADt</td>
<td>4.3</td>
<td>-</td>
</tr>
<tr>
<td>Na2SO4</td>
<td>ton/d</td>
<td>11.7</td>
<td>8.7</td>
</tr>
<tr>
<td></td>
<td>kg/ADt</td>
<td>5.9</td>
<td>4.4</td>
</tr>
<tr>
<td>NaOH</td>
<td>ton/d</td>
<td>7.3</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>kg/ADt</td>
<td>3.7</td>
<td>5.8</td>
</tr>
</tbody>
</table>
Comparing ARC and leaching processes with the same Cl and K target for (virgin liquor / ESP ash) chloride and potassium concentrations:

- Make up chemical costs for ARC is lower due to higher removal efficiency
- Electrical power consumption is about same
- Heat consumption in leaching is much lower
- Different secondary heat sources (green liquor flash steam, integration with black liquor evaporator) can be utilized in ARC
- Investment cost for leaching is lower

Summary

The liquor cycles in modern pulp mills are well closed meaning increased NPE concentrations also in black liquor. Investment in high energy recovery boiler with high power production is often very feasible. Due to recent changes in cost effectiveness, caused by higher energy efficiencies and higher energy prices, more than dozen pulp mills are to-day controlling their chloride and potassium concentrations by ash leaching or crystallization.

The selection between the two processes has to be done considering:

- Chloride and potassium input
- Capacity
- Ash and black liquor composition
- Target chloride and potassium concentrations in black liquor / ESP ash
- Removal efficiency
- Investment costs
- Mill balance (sodium / sulfur)
- Make-up chemical prices
Introduction

The black liquor recovery boilers used in pulp and paper mills operating with the kraft process are critical components of those mills. These boilers generate steam that is utilized for power generation and process applications, and they are the first step in recovering the chemicals used in the pulping process. Boilers that have a lot of corrosion, cracking, and plugging issues often operate at less than optimal conditions and generally require more down time in order to address the maintenance issues. Consequently, the recovery of energy from burning of the organic components in such recovery boilers can be considerably less efficient than desired, and significant safety issues can also be introduced.

Biomass-fired boilers, other than black liquor recovery boilers, are used to produce steam from materials like hog fuel, agricultural waste, solid waste from effluent treatment, etc. The heterogeneity of the fuels as well as the often significant water content cause a variety of materials problems for boiler designers and operators.

Boilers burning pulverized coal produce steam for generation of a very significant portion of the electric power used in the United States. These boilers operate at efficiencies of about 35%, and they produce a significant amount of CO₂ as well as other pollutants. Operation at higher efficiencies would reduce the production of pollutants, but the relatively significant sulfur and chlorine content of most coals cause serious materials problems. To be able to operate at higher efficiencies, stronger, more corrosion resistant materials would be needed.

The need for better materials for heat transfer surfaces, and particularly for superheater tubes, is a common issue that must be addressed in order to overcome the corrosion problems that are barriers to achieving higher efficiency performance. This paper describes the issues associated with recovery boiler superheater tubes and reviews industry’s experience with various materials. It also provides information about the materials problems with other types of boilers.

Background and Experience with Superheater Corrosion in Current Generation High Pressure Chemical Recovery Boilers

Corrosion of superheaters is generally not an issue in recovery boilers that are operated at a steam temperature below 450°C [1]. In current generation high pressure (HP) boilers, steam temperatures are somewhat higher, usually ranging from 480 to 500°C. It is generally accepted that accelerated corrosion of superheaters in a HP recovery boiler is mainly caused by molten salt attack [1-5]. Molten salts are generally a good fluxing agent effectively removing protective metal oxide scale from an alloy surface. Accelerated corrosion on the unprotected surface proceeds primarily by oxidation, which is then followed by dissolution of metal oxides in the molten salt.

Superheater deposits consist mainly of sodium sulfate (Na₂SO₄) and sodium carbonate (Na₂CO₃) with small amounts of sodium sulfide (Na₂S), sodium chloride (NaCl) and similar potassium (K) salts [1,6]. The first melting temperature (FMT) of the deposit depends on the composition of potassium, carbonate (CO₃²⁻) and sulfide (S²⁻), typically ranging from 520°C to 580°C [6]. Another critical factor is the proportion of liquid phase present at the FMT, which strongly depends on the chloride concentration [7]. Reported field studies and
operating experience consistently show that the corrosion rate of superheater tubes increases rapidly when the FMT of the deposit is exceeded, and more so if the molten deposit contains sulfide or reduced sulfur compounds [2,8-13]. In the past, many superheater corrosion problems were caused by molten acidic sulfate deposits containing sodium and potassium bisulfate [(Na,K)HSO₄] and pyrosulfate [(Na,K)S₂O₇] salts, which are stable at elevated concentrations of acidic sulfur gases (SOₓ) [14]. However, typical SOₓ levels produced with current operating practices are generally not high enough to promote corrosion by the formation of these molten acidic sulfate salts [3].

Superheater design for low pressure (< 6,000 kPa), (LP), recovery boilers traditionally has been governed by the need to achieve a balance between performance (steam temperature and pressure) and plugging. Relative to other boilers, recovery boilers have a much higher particulate flux through the superheater section and, consequently, tend to plug more easily [15]. Side-to-side spacing (across the bank), tube size and mechanical design (including support) has varied throughout the decades to accommodate overall boiler design [16,17]. Low alloy steels have been commonly used for superheater tubes in LP boilers, with the selection generally governed by similar design constraints as for other types of boilers, namely high temperature strength, creep resistance, oxidation resistance and economics. Table I identifies steels used along with the recommended maximum allowable tube temperature.

For superheaters in HP recovery boilers, a balance between performance, plugging and corrosion is required. With respect to corrosion, a key superheater design constraint is to maintain tube temperatures below the first melting point of the deposits. Temperatures are reduced by ensuring relatively low flue gas velocity, ensuring relatively high steam flow through each tube, arranging for the coolest steam to flow through tubes exposed to hottest flue gas, and locating the majority of the superheater sections behind the bull nose (furnace arch), shielded from direct radiation [16,17]. This design philosophy has permitted the widespread use of the less-expensive low alloy steels as superheater tube materials. However, such application has not been without problems. Reported experience with HP superheaters fabricated entirely of low alloy steel, revealed rapid corrosion at the bottom bends, with measured rates ranging from 0.3-0.6 mm/y [2,8,13] to as high as 3.9 mm/yr [19]. The cause in each case was attributed to elevated temperatures of the lower bends. Based on the various resistances to heat transfer, the surface temperature of a superheater tube is expected to be about 30°C to 50°C hotter, or higher if affected by direct radiation, than the steam temperature inside the tube [20,21]. In addition, the tube temperature may be 20°C hotter on the windward side than on the leeward side [12]. Note also that the individual tube steam temperature can vary ± 23°C from the average across the steam manifold [22]. The resultant combined increase may be beyond the FMT of the deposit depending upon the composition.

### Table 1. Typical Superheater Tube Materials in LP/HP Kraft Recovery Boilers.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Nominal Composition (wt.%)</th>
<th>Max. T1</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASME</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA-209T1A</td>
<td>K12023</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>Fe (-)</td>
<td>Cr (-)</td>
</tr>
<tr>
<td></td>
<td>Ni (-)</td>
<td>Mo 0.44-0.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C 0.15-0.25</td>
</tr>
<tr>
<td>SA-213T11</td>
<td>K11597</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>Fe 1.0-1.5</td>
<td>Cr (-)</td>
</tr>
<tr>
<td></td>
<td>Ni (-)</td>
<td>Mo 0.44-0.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C 0.05-0.15</td>
</tr>
<tr>
<td>SA-213T22</td>
<td>K21590</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>Fe 1.9-2.6</td>
<td>Cr (-)</td>
</tr>
<tr>
<td></td>
<td>Ni (-)</td>
<td>Mo 0.87-1.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C 0.05-0.15</td>
</tr>
<tr>
<td>SA-213T91</td>
<td>K90901</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>Fe 8.5-9.5</td>
<td>Cr (-)</td>
</tr>
<tr>
<td></td>
<td>Ni (-)</td>
<td>Mo 0.85-1.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C 0.08-0.12</td>
</tr>
<tr>
<td>SA-213T304</td>
<td>S30400</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>Fe 18.0-20.0</td>
<td>Cr 8.0-11.0</td>
</tr>
<tr>
<td></td>
<td>Ni (-)</td>
<td>Mo (-)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C 0.08 Max</td>
</tr>
<tr>
<td>SA-213TP347H</td>
<td>S34709</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>Fe 17.0-20.0</td>
<td>Cr 9.0-13.0</td>
</tr>
<tr>
<td></td>
<td>Ni (-)</td>
<td>Mo (-)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C 0.04-0.10</td>
</tr>
<tr>
<td>SA-213TP310H</td>
<td>S31009</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>Fe 24.0-26.0</td>
<td>Cr 19.0-22.0</td>
</tr>
<tr>
<td></td>
<td>Ni (-)</td>
<td>Mo (-)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C 0.04-0.10</td>
</tr>
<tr>
<td>SB-407-800H</td>
<td>N08810</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>Fe 19.0-23.0</td>
<td>Cr 30.0-35.0</td>
</tr>
<tr>
<td></td>
<td>Ni (-)</td>
<td>Mo (-)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C 0.75 Max</td>
</tr>
<tr>
<td>Sanicro™ 28</td>
<td>N08028</td>
<td>Bal.</td>
</tr>
<tr>
<td></td>
<td>Fe 27.0</td>
<td>Cr 31.0</td>
</tr>
<tr>
<td></td>
<td>Ni 3.5</td>
<td>Mo 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C 0.02 Max</td>
</tr>
</tbody>
</table>

1 Recommended maximum use temperature for superheater tube use in fossil-fired boilers [18].
2 Nb/Ta content of not less than eight times the carbon content and not more than 1.0 wt.%.
3 Fabricated as a co-extruded composite tube; exterior layer over an SA-213T22 core.
4 n/r = Not Reported
Replacing the low alloy steel lower tube bends with higher chromium-containing, more corrosion-resistant alloys has been one approach used to address the accelerated corrosion observed. A listing of the more typical alloys used is also provided in Table 1. The selection of these alloys was based largely on prior field testing using air-cooled probes [2,8-13]. Reported experiences of using these upgrades have been positive for the most part. A summary of preliminary experience (no more than seven years service) of austenitic stainless steel lower tube bends installed in Finnish HP recovery boilers (480°C/8,000 kPa superheater units) was published some time ago [23,24]. As reported, the corrosion rate of the installed tube bends, fabricated from Type 304, 304L, 321 and 347, stainless steel, was around 0.1 mm/yr, with no significant differences found between the various grades of stainless steel used. There are also limited reports of low corrosion rates observed on Alloy 800H lower tube bends installed in Canadian HP recovery boilers (482°C/6,200 kPa superheater units); one based on a little more than two years of service [10], and the other based on about twenty years of service [25]. Furthermore, no corrosion was reported for Type 310 stainless steel weld-overlaid composite tube bends after twenty four months of service when installed in a South American HP recovery boiler (432°C/6,400 kPa superheater unit) [19], or for Alloy 28 co-extruded composite tube bends after twelve months of service when installed in a Canadian LP recovery boiler (400°C/4,300 kPa superheater) [26].

However, there have been reported cases in which these alternatives have experienced accelerated corrosion. A summary of these cases is provided in Table 2. A reported case of accelerated corrosion exists for each of the major alloys used as replacement upgrades, with the exception of Alloy 28 lower superheater tube bends. Alloy 28 tube bends have been installed in Swedish, Brazilian and Finnish HP recovery boilers since 1994 [27]. An elevated tube temperature was identified as the root cause of the accelerated corrosion in each of the reported cases. This conclusion is consistent with the findings of the air-cooled probe studies, which show that corrosion of these alternative alloys increases rapidly when the first melting point of the deposit is exceeded [2,8-13].

In addition to the fireside corrosion issues noted above, the reliability of superheaters in recovery boilers is also strongly affected by stress-related factors. Given that the superheaters are suspended through the roof and hang freely in the flue gas environment, they are susceptible to a combination of mechanical and thermal stresses, static and/or cyclic, during start-ups, operation and shut-downs. As recently discussed, these problems can result in distortion (in-plane and out-of-plane) of the assembly, cracks at attachments, or crack-induced tube leaks [29]. Another cause for concern is waterside stress corrosion cracking. As reported in the literature, the monolithic authentic stainless steel tube bends are likely more susceptible [30].

### Table 2. Reported Cases of Accelerated Lower Tube Bend Corrosion of Replacement Alloys.

<table>
<thead>
<tr>
<th>Tube Alloy</th>
<th>Design Steam T (°C)</th>
<th>Design Steam P (kPa)</th>
<th>Tube T (°C)</th>
<th>Deposit FMT (°C)</th>
<th>Rate (mm/yr)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA-213T304</td>
<td>480</td>
<td>8,000</td>
<td>N/R</td>
<td>N/R</td>
<td>N/R</td>
<td>[11]</td>
</tr>
<tr>
<td>SA-213T304</td>
<td>480</td>
<td>6,500</td>
<td>N/R</td>
<td>N/R</td>
<td>N/R</td>
<td>[11]</td>
</tr>
<tr>
<td>SA-213TP347H</td>
<td>480</td>
<td>8,000</td>
<td>N/R</td>
<td>N/R</td>
<td>2.4-3.6</td>
<td>[24]</td>
</tr>
<tr>
<td>SA-213TP347H</td>
<td>480</td>
<td>8,000</td>
<td>N/R</td>
<td>N/R</td>
<td>0.3-1.6</td>
<td>[24]</td>
</tr>
<tr>
<td>SA-213TP347H</td>
<td>480</td>
<td>8,000</td>
<td>N/R</td>
<td>N/R</td>
<td>1.5</td>
<td>[24]</td>
</tr>
<tr>
<td>SA-213TP347H</td>
<td>482</td>
<td>8,620</td>
<td>&gt;590</td>
<td>520</td>
<td>1.0-2.0</td>
<td>[12]</td>
</tr>
<tr>
<td>SA-213TP310H/SA-213T22</td>
<td>454</td>
<td>6,200</td>
<td>&gt;590</td>
<td>560</td>
<td>1.0-2.0</td>
<td>[28]</td>
</tr>
<tr>
<td>SB-407-800H</td>
<td>482</td>
<td>6,200</td>
<td>N/R</td>
<td>N/R</td>
<td>0-1.4</td>
<td>[25]</td>
</tr>
</tbody>
</table>

*N/R = Not Reported.
Superheater Corrosion and Control in Next Generation HT/HP Recovery Boilers

Next generation HT/HP recovery boilers, which are operated at a steam temperature of 500°C to 515°C and a steam pressure of 9,900 kPa to 10,900 kPa, already exist in Japan [31-34]. Key design features implemented that help control superheater tube corrosion are reported by the boiler manufacturer to include the installation of non-process element (NPE), namely potassium and chlorine, removal equipment downstream of the recovery boiler, use of special austenitic (25Cr-14Ni) stainless steels, and a large number of sootblowers. Reducing the potassium and chlorine content in the liquor cycle should help to control corrosion by lowering the potassium and chlorine content in the deposits that form on the superheater tubes, which in turn increases the FMT [6] and decreases the proportion of the liquid phase present [7], respectively. The special stainless steels were developed with input from laboratory studies, as well as from operating experience [31,35,36]. Table 3 documents the nominal compositions of the three grades developed. The original grade YUS170 was used in early HT/HP recovery boilers. The latest grade MN25R was developed to improve the strength at high temperatures and to increase the (intergranular) corrosion resistance. Experience reported has been positive with these alloys, except when there has been contact with a high sulfur dioxide (SO\textsubscript{2}) concentration in the flue gas, [33]. There was no mention of a waterside stress corrosion cracking concern. It is noted that no independent confirmation of boiler operation and/or superheater tube performance has been reported in the public domain.

The recent interest in implementing the next generation HT/HP recovery boilers in Finland and North America has also initiated laboratory-based research and development programs designed to identify more corrosion resistant alloys from which to fabricate superheater tubes [4,37-41], in addition to those conducted in Japan [31,35,36]. An overview of the alloys and testing conditions studied is provided in Table 4. As the summary shows, a wide range of alloys have been tested in a significant number of salt mixtures, exposed to a wide range of cover gas mixtures, for several different time periods.

In spite of the many differences among the testing parameters, these studies have generated a reasonably consistent set of results, and thus conclusions can be drawn regarding corrosion above the FMT. Major findings are summarized as follows. Corrosion increases significantly at temperatures above the FMT, the extent of which increases with the amount of molten phase present at a given temperature. The corrosion mode is mostly localized (pitting and intergranular attack), consistent with a mechanism involving attack by a molten chloride-containing salt, and does not require an interaction with SO\textsubscript{2} or HCl in an O\textsubscript{2}-containing gas phase. Alloys with higher chromium contents have a higher corrosion resistance which further increases if molybdenum and nitrogen are present as additional alloying elements. Finally, the removal of NPE (potassium and chlorine) from the chemical recovery process is a critical part of corrosion control.

In contrast, the conclusions drawn from these studies regarding the corrosion of alloys below the FMT are more controversial. There is a consensus that the risk of corrosion below the FMT by the so-called “active-oxidation” mechanism [42,43] is low for the set of alloys studied, with the exception of the low alloy steel grade SA-213T22. Active oxidation involves the formation of Cl\textsubscript{2}/HCl gas within a chloride-containing deposit, which then migrates to the alloy/scale interface where the partial pressure of oxygen is low, and then reacts to form volatile metallic chlorides. As the vapor pressure of the metallic chloride products is considerable at the typical heat transfer surface temperatures involved, continuous sublimation occurs, and the gaseous metallic chlorides diffuse towards the scale/flue gas interface. Upon reaching regions with high oxygen (O\textsubscript{2}) partial pressures, the gaseous metallic chlorides react with O\textsubscript{2}/water vapor (H\textsubscript{2}O) to form solid oxides, releasing Cl\textsubscript{2}/HCl.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Nominal Composition (wt.%)</th>
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<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>YUS170</td>
<td>Bal.</td>
</tr>
<tr>
<td>HR-2EL</td>
<td>Bal.</td>
</tr>
<tr>
<td>MN25R</td>
<td>Bal.</td>
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ing scale is almost detached from the substrate and offers little protection. Two studies [37,44] conclude that, below the FMT, KCl-containing recovery boiler deposits are more corrosive than NaCl-containing ones, whereas others report the opposite result [45,46]. Another controversy involves the critical temperature at which active oxidation initiates for stainless steel alloys. Based on a laboratory test, corrosion of stainless steel by active oxidation was found to be moderately dependent on temperature in a range from 550°C to 650°C, and strongly dependent on temperatures in excess of 650°C [47]. However, a recent study documenting the corrosion of high alloy superheater tubes in a waste-wood fluidized-bed boiler shows the critical temperature may be as low as 500°C for stainless steel [48].

As the literature points out, there are many critical factors that influence the corrosion resistance of superheater tube alloys, both above and below the FMT of a typical deposit in a HT/HP recovery boiler. In spite of the relevant field studies conducted in HP recovery boilers using air-cooled probes and laboratory studies conducted under controlled conditions, it remains difficult to directly compare the corrosion resistance of candidate tube alloys. Comparisons among the field test results reported are not reliable considering the variable, poorly-defined, albeit real, environmental conditions encountered within the various boilers under study. Comparisons among the controlled laboratory test results reported are not reliable as a consequence of the differences in the testing parameters. Among the documented lab tests, it is difficult to assess, in a quantitative manner, the relative effect of elevated temperature, time at temperature both below and above the FMT, and gas composition, for a given deposit composition and alloy. In addition, more information is required on the possible influence of water vapor (H2O) on corrosion both above and below the FMT. This is important since sootblowing can increase the local H2O concentration by 3.5 vol.% [49]. Dissolved H2O in molten chloride-containing salts has been reported to enhance melt

<table>
<thead>
<tr>
<th>316, 321, 347 YUS170</th>
<th>NaCl</th>
<th>K</th>
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<th>S</th>
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<tr>
<td>10%</td>
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<tr>
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<td>K</td>
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<td>16.2%</td>
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<td>457, 310, 625</td>
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<td>Na2CO3</td>
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<td>KCl</td>
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<td>Na2CO3</td>
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<td>6.5%</td>
<td>34.5%</td>
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<td>59.0%</td>
<td>7.3%</td>
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<tr>
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<td>0%</td>
</tr>
<tr>
<td>SAN28, HR11N,</td>
<td></td>
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<tr>
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<td>Temperature: 480-520°C</td>
<td>Time: Not Reported</td>
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<tr>
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<tr>
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<td>Time: 0.2-44 Hours</td>
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<tr>
<td>Gas: N2 &amp; (4%H2-1%H2S</td>
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<td>Time: 336 Hours</td>
<td></td>
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<td>Gas: Air</td>
<td>Temperature: 450-600°C</td>
<td>Time: 188 Hours</td>
<td></td>
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</table>

Table 4. Laboratory Superheater Tube Corrosion Testing for HT/HP Recovery Boilers.
Corrosivity [39,45]. Also, in recently reported corrosion tests, water vapor additions (2 vol.%) were found to increase the corrosion rate of chromium-containing, nickel-based alloys tested in a simulated reducing low nitrogen oxide (NOx) coal-fired combustion environment [50,51]. This finding may be relevant in HT/HP recovery boilers under conditions of high carryover.

Superheater Corrosion in Biomass-Fired Boilers

Although the chemical environment in Kraft recovery boilers is much different than in boilers burning other types of biomass fuel, there are some common issues, and it is instructive to examine a few of the problems encountered when burning biomass other than black liquor. As it is for black liquor recovery boilers, specification of superheater materials for biomass boilers is challenging compared to coal and petroleum-fired utility boilers. Principally, this is due to the variety of biomass available for combustion, along with the wide range and nature of the contaminants present in the fuel. While nearly all biomass fuels are vegetative in nature, the term includes such diverse sources as wood and bark, waste agricultural debris, peat, construction waste, solid wastes from effluent treatment plants and organic refuse diverted from urban landfills, as well as black liquor.

Relative to coal and petrochemical-based fuels, biomass fuels are quite heterogeneous in nature and generally have significant water content – higher than 60 wt% in some cases. The ratio of hydrogen to carbon is higher than for coal, and biomass contains more volatile components. On average, the distribution of elemental contaminants in biomass fuels is different than for coal and includes alkali earth metals such as sodium, potassium, and silicon, chlorine and nitrogen. Urban biomass, in particular, may also contain unusual amounts of heavy metals like cadmium, lead, zinc, chromium and nickel. A critical difference between biomass and other fuels is the sulfur content, or more specifically the sulfur to chlorine ratio in the fuel. With a few exceptions, this ratio is generally much lower in biomass fuels than in coal. Properties and chemical analyses of biomass fuels have been documented by many authors; a very comprehensive summary for many forms of natural biomass can be found in an NREL-issued report [52].

As with recovery boilers, a number of damage mechanisms are operative in biomass-fired boilers. Rapid fluxing of the metal surface happens when the FMT of deposits on the tubes is exceeded, and is a potential failure mode. Potassium and chlorine are key melting point depressants familiar to operators of recovery boilers, but some heavy metal chlorides have extremely low FMTs and these are readily formed in deposits of boilers used to burn urban biomass. Corrosion of tubes in many biomass boiler superheaters has been attributed to attack by alkali chlorides (principally KCl), most likely via active oxidation, although as with recovery boilers, there remains considerable speculation about the details of the mechanism. Erosion-corrosion is also a mode of failure, although not common in superheater tubes. Silica, sand, and other hard particulates are common contaminants brought into the boiler with the fuel. These, along with residual bed media from bubbling fluid bed or circulating fluidized bed boilers, can be entrained in the flue gas passing through the boiler.

A comprehensive body of results from laboratory and field trials was published on the corrosion consequences of firing straw in utility boilers largely based on anticipated increases in superheater corrosion when utility boilers began widespread use of straw as a fuel in Denmark [53-56]. Relative to other biomass, straw can contain fairly large amounts of potassium and chloride, and it is these elements that were singled out as contributing to rapid corrosion in straw-fired boilers. Data for alloys ranging from 10CrMo910 ferritic steels to nickel-base A625 are provided in these reports, based on both in situ probe exposures for as long as 3000 hrs and steam-cooled test superheater loops installed in boilers [57-58]. From a materials point of view, a key finding was that superheater corrosion rates were found to be negligible as long as steam temperatures are kept below 470°C. This mirrors long-standing practice in recovery boilers, and although the chemical environments differ, suggests some common aspects of how protective oxides are broken down in service. An observation arising from the program was that at higher temperatures, alloys with intermediate chromium content (between about 16-18 wt% Cr) offered better overall corrosion resistance than alloys with less or more chromium, although drawing such a conclusion is somewhat empirical, since the data comes from exposures of a diverse range of commercial ferritic and austenitic alloys that differ in many aspects other than the chromium content.

Maintaining a sulfur to chlorine ratio of at least 2.0 and preferably over 4.0, has been suggested as
a means of controlling corrosion in biomass boilers by forcing sulfation of alkali chlorides before they condense on tube surfaces [59]. Due to constraints on sulfur emissions and the need to avoid possible downstream dewpoint corrosion, this approach is likely only to be effective when the total chlorine content of the fuel is low. Support for this measure was demonstrated in follow-on studies in the Danish program, which looked at the influence on corrosion of co-firing straw and coal in different proportions. Corrosion rates of TP347 SS resulting from firing fuel mixtures containing 10-20% straw in coal were about the same as firing coal, except at higher tube metal temperatures for the 20% straw/coal mixture, where formation of a potassium sulfate/iron sulfate eutectic melt was suspected of causing corrosion rates to increase [56].

In comparison to straw, wood contains much less potassium and chloride, and field studies have demonstrated that superheater corrosion rates are not nearly as rapid in wood-fired boilers [60]. Nonetheless, bark and foliage are enriched in chlorine and potassium, and even small amounts in the fuel can eventually lead to significant corrosion of superheater tubes. In such cases, mixing the woody fuel with peat (containing higher amounts of sulphur) proved beneficial in preventing formation of alkali chlorides in the flue gas [61].

In some coastal communities, logs are sea-floated to mills for processing and the bark and sapwood from these logs can contain up to 4 wt% chloride on a dry basis. When used as a fuel in boilers, this contaminated bark has been demonstrated to cause severe corrosion [48]. This latter example serves as somewhat of a precautionary note, because materials selection in the superheater for the boiler in question were made with the knowledge that elevated levels of potassium and chlorine were present in the fuel, and that active oxidation was a likely corrosion mechanism. T22 was chosen for portions of the superheater where tube surface temperatures were predicted to be lower than 465°C, while SS310H was chosen for hotter loops. The maximum superheater tube surface temperature in this boiler was predicted to be about 505°C, well under the supposed safe limit of 550°C for SS310H based on existing literature. Degradation of the SS310H tubes in the hottest loops was observed after only 18 months operation and the first tube failure occurred within 36 months. Damaged SS310H tubes were replaced with either weld overlay A625/T22 composite tubes or A625/T22 co-extruded tubes. These fared little better, with severe corrosion observed within 31 months. In addition, longitudinal through-cracking of the A625 layer on the co-extruded tubes was observed after 24 months. Subsequent investigations found tube surface temperatures of the affected loops at the steam header to be quite variable, and peak values (575-618°C) measured at those points – not at the hot ends of the loops – were well in excess of those predicted in the boiler design. It should also be noted that despite co-burning the contaminated bark with effluent sludge containing large amounts of sulfur, the S:Cl ratio in the fuel would never have reached a value sufficient to completely sulfate the alkali chlorides on formation; in fact deposit analyses found (Na,K)Cl to be as much as 50 wt% of mature deposits removed from the surface of tubes.

Corrosion of Pulverized Coal-fired Boiler Superheater Tubes
As is the case with other types of boilers, coal-fired power plants in the United States are under increasing pressure to improve their efficiency in order to provide affordable electric power to a continually growing population. At the same time, more stringent air quality regulations require significant reductions in emissions. Consequently, fossil fuel-fired power plants are subject to the same pressures as other plants - operate at higher steam temperature and pressure to achieve higher efficiency and reduce emissions of carbon dioxide and other pollutants. The target conditions for advanced ultra-supercritical (AUSC) coal-fired power plants are operation at steam temperatures as high as 760°C (1400°F) and steam pressures of at least 35 MPa (5000 psi). Operation at these conditions would significantly improve plant efficiency and reduce carbon dioxide emissions compared to conventional pulverized coal-fired power plants. However, operation at these conditions presents a significant challenge to boiler manufacturers and alloy developers since improvements in high temperature strength and fireside corrosion resistance would be required of the alloys used for superheater tubes.

Increasing steam temperatures would greatly increase the efficiency of coal-fired power plants; however, such increases in temperature can have other implications, such as adverse effects on fireside corrosion. The severe fireside wastage seen in pulverized coal-fired boilers is typically caused by a deposit-induced liquid phase corrosion mechanism referred to as coal ash corrosion. The rate for coal ash corrosion generally increases very rapidly with temperature up to about 735°C (1355°F), after which the wastage rates tend to
Coal ash corrosion is caused by the formation of molten alkali iron trisulfates on superheater and reheater tube surfaces [62-66]. Reid [65] and Kihara [67] have described the process by which coal ash corrosion occurs as beginning with the deposition of alkali sulfates on the leading sides of superheater tubes. Because of the increasing temperature gradient, the outermost material becomes sticky and captures particles of fly ash. Potassium and sodium sulfates are concentrated at the metal surface along the edge of the deposit band where metal temperatures are typically in the range of about 595-740°C (1100-1360°F). The sulfur compounds in the ash will form SO2 by thermal dissociation and catalysis of this SO2 by the Fe2O3 will produce SO3. Reaction of SO3 with metallic oxides and alkali sulfates will result in the formation of molten alkali-iron trisulfates at the metal interface through the reaction:

\[ \text{Fe}_2\text{O}_3 + 3(\text{K,Na})_2\text{SO}_4 + 3\text{SO}_3 = 2(\text{K,Na})_3\text{Fe}({\text{SO}_4})_3 \]

These molten alkali sulfates flux the protective oxide species from the surface thus accelerating oxidation and sulfidation of the alloy. Wastage of the superheater tubes is influenced by both temperature and the composition, so the traditional approaches to minimizing coal ash corrosion include using coals with lower alkali and sulfur content, limiting steam temperature, improving boiler design, using more corrosion resistant alloys and providing protective baffles around the tubes in locations that make them the most susceptible to corrosion.

As far as the selection of corrosion resistant alloys, the general rule is that the higher the chromium content the more resistant the alloy. For mildly corrosive coal ash environments, type 347 stainless steel has been found to provide adequate corrosion resistance. However, for more corrosive environments, more corrosion resistant alloys with chromium content in the 22-27% range would be required. Because AUSC boilers will operate at considerably higher temperatures (and pressures) than are anticipated for the most advanced recovery boilers, strength and creep resistance, in addition to corrosion resistance, are important considerations in the selection of superheater materials. Consequently, the emphasis for superheater tube materials has been on advanced austenitic and nickel-based alloys which have been developed to have much improved strength at the desired operating temperature.

### Recent Studies of Recovery Boiler Superheater Corrosion

Since superheater tubes in black liquor recovery boilers are not subjected to the mechanical loads anticipated for AUSC, there are differences in the materials requirements. Both types of boilers along with many biomass fired boilers have the potential for subjecting the superheater tubes to molten phases that can serve as a flux that promotes loss of the protective oxide. Two fairly recent studies have investigated the performance of selected alloys both above and below the FMT of superheater deposits through laboratory studies and exposure of corrosion probes in operating recovery boilers [40,41,68].

These studies (summarized in Table 4) had many differences but also notable similarities in part because of efforts at collaboration between the respective researchers. For instance, both projects evaluated six alloys, three of which were common to both studies. The laboratory studies for both projects involved exposing metallic samples to a selection of salts using exposure temperatures both above and below the FMT of the salts. The Finnish study used six different salt mixtures while the North American study used only one. On the other hand, the Finnish study used air as an oxidizing cover gas while the North American study used two different gases - nitrogen as a relatively inert gas and a reducing mixture containing hydrogen sulfide. The Finnish study was conducted at six temperatures ranging from 340 to 600°C while the North American study only considered three temperatures over a much more narrow range - 510 to 560°C. Both studies were conducted for relatively short times - the Finnish study lasted for one week (168 hours) while the North American study was carried out for two weeks (336 hours). Both studies considered the thickness of the corrosion product layer as a measure of the extent of reaction and from that estimated an annual corrosion rate. The North American study also considered weight change and used elemental analysis of cross sections to assess changes in surface...
composition as a result of exposure to corrosive environments. Consequently, the two studies produced some information that was complementary but also some that was unique.

Both studies also utilized field exposures of corrosion probes in operating recovery boilers. In both studies, air cooling was used in an effort to develop a temperature gradient along the probe so that there were samples exposed to temperatures both below and above the first melting temperature that was measured for deposits recovered from the respective boilers. Two probes were exposed in the Finnish study; each for a little less than 700 hours. The North American study successfully exposed only one probe, but it was exposed for 1000 hours. Both studies utilized advanced analysis techniques to examine samples exposed in these probes. The Finnish studies utilized a scanning electron microscope to examine cross sections of their probe samples while the North American study examined their cross sectioned samples with an electron microprobe.

An example of results from the North American laboratory corrosion studies is given in Fig. 1 which shows the measured weight loss of samples as a function of temperature. The samples were embedded in a salt mixture with a FMT of 525°C and a reducing cover gas containing hydrogen sulfide. Exposure temperatures were 510 and 560°C, but no T91 sample was exposed at the higher temperature. The samples were exposed for 336 hours, and these results show higher corrosion rates above the FMT but increasing the chromium content decreases the corrosion rate for these conditions. Figure 2 shows the effect of the cover gas on the calculated corrosion rate for samples embedded in salt and exposed at 510°C (below the FMT) for 336 hours. It is clear that the reducing, hydrogen sulfide containing cover gas leads to significantly higher corrosion rates for nearly all the samples.

For samples exposed on a corrosion probe in the superheater area of an operating recovery boiler, the extent of attack was measured on samples exposed above and below the FMT. The results shown in Fig. 3 indicate that the below the FMT the total depth of attack decreases with increasing chromium content. However, above the FMT the depth of attack does not correlate with the chromium content. Clearly other factors play a significant role in developing an alloy’s corrosion resistance. Micrographs of cross-sections of the five samples exposed at the highest temperatures are shown in Fig. 4. The extent of subsurface attack is clearly seen on these samples.

**Summary**

The three types of boilers discussed in this paper, chemical recovery boilers, biomass-fired boilers and pulverized coal-fired boilers, all have limitations on their operating temperatures and pressures because of issues with degradation of high temperature components, particularly superheater tubes. Corrosion by a molten phase that forms on the tubes and fluxes the normally protective oxide is a common problem as well as corrosion by gaseous species that typically contain sulfur and/or chlorine compounds.

For service below the FMT of the corrosive phase, the active oxidation mechanism is apparently operative, but using alloys with higher chromium concentrations generally provides some solution to the corrosion issue.

For service above the FMT, more highly alloyed metals are required but use of alloys with higher chromium content does not necessarily reduce the corrosion rate.

Additional, more extensive studies, both laboratory and field, are needed to gain a better understanding of the variables that affect superheater tube corrosion and to better determine the best means to control this corrosion to ultimately permit operation of recovery boilers at higher temperatures and pressures.
Acknowledgements
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References
23. P-E. Ahlers, A. Jaakola, “Experiences of
Figure 1. Weight loss measured after exposure to the synthetic salt mixture with the reducing cover gas (H₂S-H₂-H₂O-N₂) for 336 hours at 510°C (below FMT) and 560°C (above FMT) [40].
Figure 2. Annual corrosion rate (extrapolated from 336 hour weight loss) for selected alloys immersed in the synthetic salt mix and exposed at 510°C to N₂ cover gas or to the reducing gas mixture H₂S-H₂-H₂O-N₂.

Figure 3. Depth of attack (measured from micrographs) for samples from the corrosion probe that was exposed in a recovery boiler for 1000 hr. The estimated average exposure temperature is indicated, as squares, showing whether samples were above or below the FMT [40,68].
Figure 4. Micrographs from cross-sections of the five hottest samples on the corrosion probe showing the outer surface on the “bottom” side [68].
ECONOMIZER LEAK STUDY

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Introduction

The AF&PA Recovery Boiler Committee looked at the number of economizer pressure part failures in the recovery boilers. Economizer failures remain a significant cause of boiler downtime in the industry. No recovery boiler explosions have been directly attributed to economizer failures. Yet, there is a risk of an explosion in those economizer arrangements where water from an economizer failure could enter the furnace cavity. Not all economizer failures have been reported to BLRBAC. Thus the magnitude of the problem may be underestimated. Although the root causes of some economizer pressure part failures are known, the information has not been widely disseminated. No systematic study of economizers has been made. The AF&PA Recovery Boiler Committee realized the need for an industry-wide effort to review economizer tube failures, to collect and analyze available information on economizers. Dr. Tom Grace and Mr. Jack Clement were contracted to study this problem.

Study

Data on economizer failures were collected from operating mills, recovery boiler suppliers and BLRBAC records. A total of 346 economizers were included in the study of which 266 were located in the US and 80 in Canada. Data were also collected from Sweden (1998 to 2001) from 41 incidents involving 12 different economizers, and from Finland (2000 – 2004). Because of the brevity of these reports, they were not used in the study.

The data were reviewed, interpreted and analyzed. The investigators met with suppliers and some operating companies to resolve some discrepancies. Additional data were obtained from detailed incident reports, equipment suppliers and operating sources. Sorting techniques were applied to the data to identify the types of failures, their frequency and how these failures relate to the design and operating variables. It was apparent that economizer design and construction play a critical role in economizer integrity. The investigators had follow-up meetings with suppliers to ascertain design details and discuss the available failures information. The overall objective of the study was to understand the causes of recovery boiler economizer failures and to identify means for preventing their occurrence. Five specific objectives were met:

- Document and evaluate the industry experience;
- Categorize the types of failures that have occurred;
- Determine the correlation of failures with design and operating factors;
- Provide Guidelines for specification and construction of economizers, and
- Provide a reference for operating and maintenance practices impacting economizers.

Findings

In analyzing the data, it was apparent that a number of specific types of failures occurred frequently. Due to the lack of detailed information in a number of incidents, it was difficult to know the extent of any given operation. It was even less clear how operating practices affect stress and fatigue cracking problems. The frequency and nature of the economizer failures were classified into a relatively small number of categories:

- stress or fatigue cracks
  - cracks in the tube – header attachments region
  - cracks in the fin terminations
  - cracks at other locations
- handhole and radiography test plug seal weld leaks
- poor quality welds, other than those above
- external tube thinning
- internal corrosion in thinning
- mechanical damage
- leaks at rolled joints.

The most widespread problem was stress and fatigue cracks near the tube-header interface. There are indications that some of these cracks originate on the waterside, but it is unclear as to what extent water-side conditions play in this role. Although it was difficult to prove, some operation conditions are clearly detrimental. A listing of operating variables that could potentially affect economizer integrity was developed. As a result of providing a listing or description of operating practices that are detrimental to the economizer, it became apparent that repair and maintenance practices were also vitally involved. Thus, a stand-alone document “Operating and Maintenance Practices Impacting Economizers” was produced.

Design details and experience information were supplied by suppliers. The investigators were able to show some conclusions from this information and the reports of economizer failures. For example, economizers installed before 1990 indicated many more leaks and about half of these leaks were attributed to handhole seal weld leaks and radiography hole plug leaks. Nearly 300 leaks occurred in the 62 economizers installed between 1980 and 1990. In the period from 1990 to 2004 where 70 economizers were installed, there were 45 leaks.

Experience shows that economizers can be operated for over 20 years without experiencing tube leaks if they are properly designed, constructed, operated and maintained. Design evolution has had a very important influence on economizer reliability. There has been a significant reduction in the frequency of economizer leaks since the adoption of the mini-header design by the suppliers in 1990. A very small number of economizers have been responsible for most of the reported leaks with the mini-header design. With the change in design and the guidelines written to consolidate the best experience, and the application of these principles can result economizers in place to operate many years without unplanned outages. Weld quality is a critical aspect of getting a reliable economizer that will last.

It was common to see a pattern of economizer leaks in a given area that were directly connected with previous leaks in that area. These might take the form of a leak in a repair weld for a previous leak, a leak in the seal weld of a tube plug, or a leak in a thinned area where a previous leak sprayed on adjacent tubes. Lack of access for making effective repairs and doing proper inspections around failure sites is a critical factor in this regard. The most serious problem in economizer today is cracks near the tube-to-header welds, most commonly at the feedwater inlet headers and the economizer discharge headers.

Acknowledgments
I would like to thank Dr. Grace and Mr. Clement for the work they have done in this project and helping me in the presentation of this study.
Gasification of black liquor has long been recognized as an interesting alternative to the conventional recovery boiler. Proponents of black liquor gasification point out its many potential advantages, including improved overall energy efficiency, enablement of advanced pulping technologies, opportunities for product diversification, potentially lower capital costs and avoidance of the smelt-water explosion risk inherent with recovery boilers. Over the past few decades, millions of dollars have been spent developing black liquor gasification technology at industrial R&D centers, national laboratories and universities. Yet, despite seemingly strong drivers and years of development, only two relatively small black liquor gasifiers are in commercial operation today, and no mills have an integrated gasification system producing biofuels or biopower.

There are many reasons that black liquor gasification technology has not achieved commercial success. Some are technical, of course. Black liquor is a challenging fuel and gasification, even for conventional fuels like coal, is still not well-established. Advances in recovery boiler design have also made that technology more efficient and competitive. Financial considerations have significantly limited development. Bringing a new technology to market is expensive, and few companies have had the resources or fortitude to progress beyond small-scale testing. Additionally, end users are reluctant to adopt a new, unproven technology so key to successful operation of the mill unless they can be sure that its availability and performance are at least on par with existing technology. Yet another challenge for black liquor gasification is shifting priorities within the pulp and paper industry and global energy markets.

This chapter explores the history of black liquor gasification development, taking into consideration the technical and economic motivations behind various technologies. Black liquor gasification is also reevaluated in the context of today’s market, which has very different priorities from those of even ten years ago, with regard to technical understanding, economics, energy production and environmental consciousness.

Changing Drivers for Black Liquor Gasification Development

Development of the first pyrolysis- and gasification-based alternative recovery processes in the 1960’s and 1970’s was driven primarily by a desire for processes that were safer and more environmentally sound than the recovery boiler. Recovery boiler explosions were an uncomfortably common occurrence during that time, with roughly 3-4 occurrences per year in North America [1], and likely twice that number world-wide. The recommended practices for safe operation and shutdown that are commonplace today were not available at that time. So, there was strong interest in developing safer recovery systems with no risk for explosion. Many proposed systems used fluidized beds to process black liquor since this eliminated the presence of molten smelt.

Improving environmental performance was another driver for development of alternative recovery systems in the 1960’s and 1970’s. In particular, there was interest in minimizing the smell associated with kraft pulping. New gasification-based technologies focused on eliminating “malodorous compounds” associated with recovery boilers were proposed [2].

In the 1980’s, gas turbine technology had advanced to the point where coal-based integrated
gasification combined cycle (IGCC) power plants were identified as being potentially superior to conventional steam turbine-based plants. It was soon recognized that similar improvements in energy efficiency could result if black liquor were processed in a gasifier integrated into a combined-cycle power generation system. It was estimated that a so-called BLGCC (black liquor gasification-combined cycle) could increase electrical production efficiency by as much as ten percentage points without affecting steam production. Spurred by the potential energy and cost savings, a surge of interest in black liquor gasification followed. The period from 1985 to 1995 was the most active in the history of black liquor gasification technology development.

The natural separation of sodium and sulfur that occurs during black liquor gasification gave rise to a new set of drivers for the technology in the 1990’s. Unlike a kraft recovery boiler, where sulfur remains bound to sodium as sulfide or sulfate, most of the sulfur in a gasifier is converted to gaseous hydrogen sulfide. The sulfur can be recovered from the gas and used at targeted locations in the pulping process. Not only does this improve control of the sodium-sulfur balance, but it enables advanced pulping technologies such as split-sulfidity pulping, which can improve both pulp yield and pulp quality. In short, integrated black liquor gasification creates opportunities to increase production of a mill’s primary product, pulp, thereby improving revenues. This continues to be a strong driver for gasification, and one which is specific to the pulp and paper industry.

In recent years, the role envisioned for black liquor gasification has changed significantly in both Europe and North America. Worldwide, there has been a push to limit emissions of carbon dioxide, which is seen as a key contributor to global warming. In the European Union countries, policy associated with this environmental consciousness has resulted in real economic incentive to reduce fossil fuel-based CO₂ emissions via the cap-and-trade system for carbon dioxide. Similar policies to put a price on CO₂ emissions are expected in the U.S. and Canada in the near future. Renewable, carbon-neutral biomass-based fuels are an attractive alternative, and can be produced through gasification of black liquor and biomass. The synthesis gas resulting from gasification is rich in hydrogen and carbon monoxide, which can be catalytically converted to a variety of biofuels, including methanol, dimethyl ether, and Fischer-Tropsch fuels. Producing transportation fuels through gasification of black liquor is not a new idea [3]. But changes in policy, environmental consciousness and instability in the cost and availability of petroleum have made production of biofuels from domestic, renewable, carbon-neutral feedstocks an attractive option. This has provided a new driver for development and commercialization of gasification technology.

Clearly, since the 1960’s incentives behind development of black liquor gasification technology have shifted as markets and priorities have changed. Yet, the drivers for black liquor gasification development are not mutually exclusive. A fully integrated black liquor and biomass gasification-based mill would be able to use advanced pulping technologies that take advantage of the sodium-sulfur split while simultaneously producing biofuels and/or biopower, all the while offering a more energy efficient, more environmentally friendly alternative to the recovery boiler. The key is to have a viable black liquor gasification technology. The following sections review development of gasification technology and summarize the state of black liquor gasification technology today.

**History of Black Liquor Gasification Development**

A recent review of alternative recovery technologies identified over twenty serious efforts to develop black liquor gasification systems over the past 40 years [4]. The technologies are about evenly split between low temperature fluidized bed-based systems and high temperature systems in which smelt leaves the gasifier in molten form. Notable technologies which were developed at least to the pilot stage are described below.

**The Copeland Recovery Process**

The Copeland process (Fig. 1) was one of the most successful alternative recovery systems of the past half century, with several installations worldwide. The process was developed by George Copeland during the 1960’s and 1970’s as a safer alternative to the recovery boiler and as an alternative to provide incremental black liquor processing capacity to a mill [5-8]. The process involved spraying liquor onto a wide, bubbling fluidized bed comprised of inert material and black liquor inorganics and fluidized with preheated air. The bed temperature was relatively low, in the range 650-750°C. Most installations were at non-kraft mills, although a relatively large (300 tpd) system for processing kraft liquor was installed in Canada. Typically,
the system was operated at or near stoichiometric conditions, so that it behaved as a black liquor combustor. Later development focused on operating the system under sub-stoichiometric (gasification) conditions and combusting the product gas in either a dedicated boiler or by co-firing in an existing boiler. Ultimately, the Copeland process lost favor as improvements in recovery boiler technology and a push towards higher energy efficiencies made the process uncompetitive.

**The SCA-Billerud Process**

SCA-Billerud of Sweden developed a relatively successful alternative recovery process in the 1960’s and 70’s [9-11]. The process (Fig. 2) involved spraying black liquor into the top of a reactor heated by an oil or gas burner, which caused the liquor to dry and pyrolyze. The temperature was kept low enough to avoid melting the ash in the liquor. The char flowed with the exiting gas through a heat recovery boiler and into a spray scrubber, where it was captured by the liquid and filtered to recover green liquor. The unburned char was mixed with fresh black liquor and recycled to the process. The pyrolysis gas was cooled to condense out water and burned in a boiler to produce steam. A 25 ton/day pilot system for kraft liquor was operated in the early 1970’s. The first commercial plant was installed in Sundsvall, Sweden in 1968 and several other plants were subsequently installed in Japan and the United States at mills as large as 1000 tons pulp/day. However, technical challenges, including buildup of ash and char in the gas passages, as well as relatively low efficiency compared to conventional technology caused interest in the SCA-Billerud process to evaporate by the mid-1970’s and no further plants were ever constructed.

**The Direct Alkali Recovery System (DARS) Process**

The DARS process was similar to the Copeland process in that black liquor was combusted in a fluidized bed reactor. Unlike the Copeland proc-

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*Figure 1. The Copeland Recovery Process [6].*

*Figure 2. SCA-Billerud process.*
ess, however, the DARS process involved addition of iron oxide to the black liquor to achieve in-situ causticizing via formation and subsequent leaching of sodium ferrite [12]. The largest DARS process was constructed in 1986 by Associated Pulp and Paper Mills at their Burnie, Tasmania soda process pulp mill, and processed roughly 150 tds/day of black liquor. Problems associated with fluidization and sodium ferrite dust formation were encountered during the first few years of operation. Nonetheless, the system was operated until the mill was shut down in the late 1990’s [13,14].

The St. Regis Hydropyrolysis Process

During the 1960’s, St. Regis Corporation developed a novel system for processing black liquor (Fig. 3). The process involved heating low-solids black liquor to roughly 330°C at approximately 200 atm pressure to produce combustible gases, a low-ash char and an alkali salt solution similar to green liquor [15-17]. The char was washed and could be used as activated carbon or fuel for a boiler. The gases evolved during the process were burned to provide heat for the system. St. Regis constructed a 16 tds/day pilot plant in the mid-1970’s, but no commercial system was ever constructed. Eventually, the hydropyrolysis process was deemed uncompetitive and development was terminated. Interestingly, about the same time that St. Regis was developing hydropyrolysis, Texaco Corporation was doing in-house work on a very similar process, which they described as a coking process [18,19]. Texaco was granted over 15 patents relating to their process, but no pilot or commercial plant was ever constructed.

VTT’s Circulating Fluidized Bed Gasification Process

The Technical Research Center of Finland (VTT) developed a pressurized air/oxygen-blown circulating fluidized bed gasifier between 1988 and 1993 [20,21]. The process operated at roughly 650°C and at pressures to 35 atm. A 200 kW development gasifier processing roughly 1.5 tds/day of liquor was constructed at a mill in Äänekoski, Finland and was tested for several years. Agglomeration of the bed was problematic, but was improved by using alumina particles as bed material. No commercial plant was ever built based on the VTT process, and development was ultimately terminated due to technical difficulties and a challenging economic climate.

![Figure 3. Diagram of the St. Regis hydropyrolysis process.](image-url)
**ABB’s Circulating Fluidized Bed Gasification Process**

ABB developed a circulating fluidized bed gasifier similar to the VTT system during the early 1990’s [22,23]. A 2.5 tds/day development gasifier was constructed at ABB’s research facility in Västerås, Sweden and ran many successful, albeit short, test campaigns over the course of several years. During later years of development, ABB recognized that addition of titanate to the black liquor offered the potential to implement in-situ causticization of the black liquor. It also increased the melting temperature of the bed solids, allowing operation at higher temperatures [24]. ABB was able to operate the gasifier at 680°C without problem and achieved good carbon conversion. ABB continued development until 1997, when the program was abandoned due to shifting development priorities and lack of a clear market for the gasifier in a reasonable time frame.

**The Swedish NSP Cyclone Gasifier**

In the early 1970’s, a team of Swedish and Finnish companies, research institutions and forest products organizations jointly developed a unique cyclone gasifier dubbed the NSP, or “Ny Sodahus Process” [25]. The cyclone gasifier operated in a manner similar to a cyclone combustor used in coal power plants, except that only about 90% of the air required for complete combustion was fed through the gasifier (Fig. 4). Additional air was fed into the main part of the boiler system. The temperature at the exit of the gasifier ranged from 1100 to 1400°C. An attractive feature of this technology was that existing recovery boilers could be rebuilt to have several cyclone gasifiers around the perimeter. Char and smelt from the black liquor would be forced to the walls of the gasifier due to the strong swirling action, so the exiting fuel gas would be relatively free of particles. The molten slag was tapped from the low end of the cyclone and fed to a dissolving tank.

In the early 1980’s a 100 tds/day NSP gasifier was installed at a mill in Karlsborg, Sweden. During the two years the system operated, it experienced severe technical problems such as cracking of the steam-cooled cyclone shell [26]. Ultimately, the NSP program was terminated due to overwhelming technical challenges and lack of continued funding.

![Figure 4. NSP cyclone gasifier. Adapted from [27].](image-url)
The Champion-Rockwell Molten Salt Gasification Process

The Champion-Rockwell molten salt gasifier (Fig. 5) was originally developed by Rockwell Corporation to process fuels such as coal. In the early 1980’s researchers at Champion Paper Corporation recognized the potential for black liquor gasification and several years of development ensued [27]. The Champion-Rockwell black liquor gasifier was a counter-flow, refractory-lined entrained-flow reactor which contained a pool of molten smelt at the bottom. Black liquor was injected at the top and flowed downwards, undergoing pyrolysis and gasification as it reacted with the upwards-flowing air. The resulting producer gas exited near the top of the gasifier and the char from the black liquor fell into the pool of smelt, where conversion was completed and sulfate reduction took place. The gasifier was hottest at the bottom, where the temperature was roughly 950°C. Several tests were performed using Rockwell’s 6 ton/day pilot gasifier [28]. Carbon conversion was good and sulfate reduction in excess of 95% could be achieved. Plans were developed for a larger, pressurized pilot gasifier [29]. But, development funding ran out and development of the Champion-Rockwell gasifier was postponed indefinitely.

MTCI/TRI’s Fluidized Bed Steam Reforming Process

Manufacturing and Technology Conversion International (MTCI) began developing a bubbling fluidized bed steam reformer (gasifier) in the mid-1980’s [30,31]. The black liquor gasification technology is now under license to ThermoChem Recovery International (TRI), which continued development until recently. The process (Fig. 6) involves injecting black liquor into a bubbling fluidized bed in which steam is the fluidizing and reacting gas. The overall steam reforming process is endothermic, so it is necessary to provide heat to the system. In the MTCI/TRI system, natural gas or syngas is combusted in a proprietary pulsed combustor and the hot exhaust gases pass through bundles of tubes immersed in the fluidized bed. The overall process is energy positive and produces a gas containing 65-70% hydrogen.

Figure 5. Champion-Rockwell pilot gasifier. [30]
In the late 1980’s, a 6 tds/day test gasifier was constructed at a recycled paper mill in Ontario, California and processed paper mill sludge. Kraft black liquor from another mill was also processed in this system during dedicated test campaigns. In the mid-1990’s, a 50 tds/day kraft black liquor gasification demonstration system was constructed at Weyerhaeuser’s New Bern, North Carolina mill [32]. This system was operated for a couple years, ultimately achieving 500 hours of continuous operation, after which it was shut down and dismantled. In 2003, a 100 tds/day MTCI gasifier was installed at a Norampac mill in Ontario, Canada, and continues to process all the mill’s liquor. In 2004, a 200 tds/day demonstration system having two parallel gasifiers was started up at Georgia-Pacific’s Big Island, Virginia mill [33]. This system experienced technical problems with the fluidized beds, pulsed heater combustors and gas cleaning system. Ultimately, Georgia-Pacific’s management determined that the system would not be able to achieve the necessary availability and the gasification system was replaced with conventional technology.

**Chemrec’s Entrained-Flow Gasification Process**

The Swedish company Chemrec began development of its high temperature entrained-flow gasification technology in the mid-1980’s, when the technology was owned by Kamyra and eventually Kvaerner. The initial concept involved plasma gasification, but the very high energy requirements necessary for the plasma guns turned favor towards partial oxidation [34]. In the Chemrec process (Fig. 7), black liquor and either air or oxygen are fed into a burner at the top of a refractory-lined reactor. Only 40-50% of the total oxygen needed for combustion is fed, resulting in an overall reducing (gasifying) atmosphere.

*Figure 6. Conceptual MTCI system configuration for kraft liquor. [32]*

*Figure 7. Chemrec gasifier.*
The liquor pyrolyzes and is gasified at roughly 950°C, producing a low to medium heating value syngas and molten smelt. The products are cooled and separated in a quench system below the reactor. The smelt dissolves in a quench bath, forming green liquor.

Chemrec has two variants of their technology, a low pressure air-blown system intended to provide incremental capacity and a high pressure oxygen-blown system targeted as an alternative to the recovery boiler. Chemrec’s first pilot plant was a 3 tds/day air-blown, atmospheric pressure system constructed in Hofors, Sweden in 1987. This plant operated well enough to prove the technical feasibility of entrained-flow gasification and a commercial 75 tds/day plant was installed in Frövi, Sweden in 1991. Five years later, Weyerhaeuser constructed a 330 tds/day system in New Bern, North Carolina [35]. Development of the pressurized system began in 1994 with a 6 tds/day air-blown pilot plant in Skoghall, Sweden. This was rebuilt to a 10 tds/day oxygen-blown system in 1997, which was operated until 2000 [36]. Based on experience from these systems, a new 20 tds/day pressurized oxygen-blown pilot was constructed in Piteå, Sweden in 2005. This system has logged more than 8000 hours of operating time and has been key to Chemrec’s technology development [37].

Other Processes
In addition to the processes described above, many more processes were proposed and tested at laboratory or bench scale, but never advanced to pilot scale. These include Paprican’s “atomization suspension technique” (AST) process (1955-1968) [38], the University of California pyrolysis-gasification-combustion process (1967-1980) [39], Weyerhaeuser’s fluidized bed dry pyrolysis process (1972-1978) [40], Tampella’s pressurized entrained-flow gasifier (1988-1993) [41], Ahlstrom’s suspension gasifier (1988-1993) [42], Babcock & Wilcox’s fluidized bed gasifier (1993-1998) [43], Noell’s entrained-flow gasifier (1996-2000) [44] and KBR’s transport gasifier (1999-2002) [45].

Current Status of Black Liquor Gasification
Today, there are two commercial black liquor gasifiers in operation. One is the air-blown, low pressure 330 ton/day Chemrec booster gasifier processing kraft liquor at Weyerhaeuser’s New Bern, North Carolina mill. The first few years of operation were associated with frequent shut-downs resulting from failure of different parts of the system, especially auxiliary systems, but performance and availability have improved significantly [35]. The main challenge with the gasifier itself was refractory degradation. Refractory lifetimes were on the order of 6-8 months and the system had to be shut down for several weeks each time the refractory had to be replaced. Over the past decade, however, research has resulted in much improved refractory materials installation designs. Consequently, the most recent materials used to line the gasifier have lasted more than two years and the gasifier is now a vital component of the mill’s recovery system. Chemrec also has a very active research program centered on their 20 tds/day pressurized pilot plant in Piteå, Sweden and is in discussion with various clients about commercial installations of this technology.

The other commercial gasifier in operation is a 100 ton/day MTCI/TRI fluidized bed steam reformer at a Norampac mill in Ontario, Canada which started up in 2003. The gasifier processes all the black liquor from this mill, which uses a carbonate pulping process. The process has a very simple configuration, almost ideal for this technology, which avoids several challenges with low temperature black liquor gasification. Black liquor is fed to a single steam-blown fluidized bed that is heated by pulsed heaters firing natural gas. The raw syngas from the system is kept hot and fed directly into a boiler for steam production. Because the syngas is not cooled, there is little opportunity for tars to condense before the gas is combusted in the boiler. Indeed, the lack of a syngas cleaning system simplifies the process enormously and removes a potential location for operational problems. Using natural gas rather than product gas from the gasification process also improves availability of the system. The Norampac gasifier continues to operate. However, due largely to technical challenges and termination of the Georgia-Pacific Big Island demonstration system mentioned earlier, TRI has placed development of their black liquor gasifier on hold and is focusing their efforts on processing more conventional biomass materials.

New Opportunities for Black Liquor Gasification
As indicated earlier, incentives for development of black liquor gasification technology have varied over the past several decades and today we are again witnessing a shift in thinking about black
liquor gasification. The high price of oil and transportation fuels in recent years has made people think seriously about alternative fuels for the first time in decades. When this occurred in the 1970’s, there was significant investment in technologies for extraction of oil from oil shale and oil (tar) sands in North America. However, today there is a heightened environmental consciousness regarding use of fossil fuels and the damaging influence of carbon dioxide and related global warming. The only renewable source from which one can produce replacement transportation fuels is biomass. In the U.S. and elsewhere, interest and investment in corn-based ethanol exploded in recent years. Similar growth has occurred with biodiesel derived from natural oils, particularly soybean oil. Unfortunately, this growth had the unintended consequence that the cost of the feedstock materials, corn and soybeans, spiked to historical highs. The high cost and reduced availability of these crops as foodstuffs severely affected regions of the world, particularly third-world countries, which are struggling to feed their populations. There is now significant interest in production of biofuels from biomass which does not involve displacement of food or cropland otherwise dedicated to food production. Production of biofuels from forest-based biomass is an obvious solution.

Among forest-based biomass, black liquor offers the best opportunity for biofuel production in the near term. It contains the most energy-rich component in the wood, lignin, and has little product value on its own. Black liquor is readily available, is very reactive so it can be processed at relatively low temperature, and it can be pumped into pressurized systems. High pressure, high temperature gasification technology is also commercially available. In comparison, handling of conventional biomass is more challenging and no pressurized biomass gasifier suitable for integration into a thermochemical biofuel production facility is currently commercially available.

**The Future of Black Liquor Gasification**

The future for black liquor gasification looks more promising today than ever. Currently, it appears that high temperature, air/oxygen-blown entrained-flow gasification has emerged as the technology of choice. This is due to the relatively simple design, good conversion efficiency, low tar production and thousands of hours of successful operation. Entrained-flow technology is now being offered commercially, marking a milestone in gasification development. The intense interest in production of non-food crop-based biofuels which has arisen from concern over global warming and energy security has produced a strong market for products which can be produced through black liquor gasification. This in turn has sparked the interest of investors. So, for the first time in the history of black liquor gasification development, three key elements for successful commercialization are in place: (1) a feasible, demonstrated technology, (2) a strong market and (3) financial support.

Within the next few years we will likely see the first integrated biorefineries incorporating black liquor gasification for thermochemical production of biofuels. Undoubtedly, these first-of-a-kind plants will experience technical problems, if not with the gasifier then with some other part of the process. The ultimate success of black liquor gasification technology will depend on how quickly any technical difficulties can be overcome. If these challenges can be resolved quickly and the biorefineries operate successfully, then the prospects for black liquor gasification are good. If, however, these first plants are plagued with insurmountable technical problems then black liquor gasification’s reputation will suffer by association, even if the problems are unrelated to the gasifier.

No matter what happens over the next few years, it is certain that in the long run priorities will continue to shift, technology will continue to advance and the economics of papermaking and energy will continue to evolve. In tandem with those changes, development of black liquor gasification technology will undoubtedly also continue as long as there is black liquor available.
References
3. Prahacs, S., Production of methanol from the organic materials present in spent pulping liquors, with the simultaneous recovery of the pulping base and sulphur values present in said liquors. Canadian Patent No. 733546 (1966).
24. Dahlquist, E. and Ringvall, T., Presentation of a dry black liquor gasification process with direct causticization developed by ABB. Olle Lindström Symposium (1997).
BIOREFINERIES FOR CO-PRODUCTION OF RENEWABLE TRANSPORTATION FUELS

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Introduction

As the 21st century proceeds, civilization faces perhaps its greatest challenges yet:
• A steady population growth, moving toward 9 billion people or more worldwide by 2050,
• An expectation for an increasing standard of living in many countries, including the most populated ones,
• An increasing appetite for raw materials, energy, and fresh water, and
• A finite or declining resource base on planet earth.

The concepts of renewability and sustainability have become recognized as essential if we are to manage these seemingly conflicting challenges, not only for ourselves, but for future generations as well.

Industries with renewable resources and the capability to convert their raw materials sustainably to valuable products are in a strong position to benefit from this capability. One of the few industries that is well positioned to provide a range of products, both new and traditional, from renewable resources is the Forest Products Industry. Opportunities abound for new materials, chemicals, fuels, and energy as well as for conventional paper, board, and consumer products.

One specific opportunity is fuels from forest biomass. We first consider alternatives for producing transportation fuels from lignocellulosic biomass. We then consider how to integrate fuels production into the forest products industry, and consider examples where this is being done.

Options for Renewable Transportation Fuels

Many fuel and energy alternatives are being considered today for renewable transportation. Figure 1 shows some of the alternative routes to transportation fuels from lignocellulosic biomass. Production of biofuels from ligno-cellulosic biomass has not yet become a significant source of transportation fuels, although the potential great. Estimates are that 25% of EU’s transportation fuels needs and 30% of the U.S.’s could be met by renewable fuels by 2030.

What Transportation Fuels should be Produced?

It can be argued that electrical vehicles will ultimately replace liquid fuel-powered vehicles [1,2]. However, the time frame for electrical vehicles to replace liquid fuel-powered vehicles would depend on several factors including improvements in electric vehicle technology, phase-out of the existing transportation vehicle fleet, and the availability of electrical power to meet transportation needs. 25 years is likely the minimum time frame for electrical vehicles to gain a dominant position if they indeed do that. In this scenario, liquid fuels must satisfy transportation needs. Which fuel or fuels will succeed depends on several factors, including
• Energy density
• Distribution system options
• Environmental impact (LCA)
• Local temperature
• Engine technology advances

Availability of Biomass Resources

In Europe: In 2006, Ericsson and Nilsson assessed the potential biomass supply in 27 countries in Europe[1]. They found that the potential supply of biomass energy amounts to up to 17.2 EJ/a, about 27% of the overall energy supply in fifteen western European countries (the EU15) in 2001. They concluded that the biomass supply target of 5.6 EJ/a in the EU15 by 2010, set by the European Commission in 1997, was clearly achievable.

In the United States: In 2005, Perlack and co-workers at Oak Ridge National Laboratory published an extensive analysis of the availability of cellulosic biomass in the U.S.[1]. This report is often referred to as “The Billion Ton Biomass Report.” It concluded that, as of 2005, 368 million t/yr of biomass is available from U.S. forests, and another 194 million t/a is available from agricultural resources. Biomass availability was projected to increase to 1.3 billion t/a by 2030, enough to generate sufficient biofuel to replace 30% of the current petroleum-derived transportation fuel. The increase in biomass availability from 2005 to 2030 was expected to come entirely from an increase in agricultural crop production including energy crops; forest residues were projected to remain constant over this time period. This underestimates the potential for increasing forest productivity.

A breakdown of the 358 million t/yr of forest residues identified in the Billion Ton Biomass study is included in Table 2. 39% of the total is either black liquor or mill residues. Most of these two potential feedstock are consumed on site by pulp & paper mills and wood processing plants to produce power and process steam. The remaining 61% are largely available although the cost of col-

Table 1, Estimated future biomass resource base for the U.S.[11]

<table>
<thead>
<tr>
<th>Biomass Resource</th>
<th>2005</th>
<th>With changes in technology</th>
<th>With technology &amp; land use changes + perennial crops</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perennial Crops</td>
<td>0</td>
<td>0</td>
<td>377</td>
</tr>
<tr>
<td>Grains &amp; soybeans</td>
<td>15</td>
<td>97</td>
<td>135</td>
</tr>
<tr>
<td>Crop residues</td>
<td>179</td>
<td>477</td>
<td>439</td>
</tr>
<tr>
<td>Forest resources</td>
<td>368</td>
<td>368</td>
<td>368</td>
</tr>
<tr>
<td>Total, t/yr</td>
<td>562</td>
<td>942</td>
<td>1319</td>
</tr>
<tr>
<td>Total, EJ/yr</td>
<td>10.6</td>
<td>17.6</td>
<td>24.5</td>
</tr>
</tbody>
</table>
lecting and transporting unmerchantable timber and harvesting residues from forests has so far limited their widespread use as biomass feedstock for fuels or power generation in the U.S.

### The Integrated Biorefinery Concept

One of the principles of sustainability is that raw materials should be utilized first for the highest value products, with residual raw material used for other, less valuable materials. Table 3 shows typical values for lumber, bleached softwood pulp, and ethanol, both per unit of material of fuel and per metric ton consumed to produce them. As expected, the order of value is lumber > pulp fiber > ethanol > power. For any reasonable combination of prices for these four commodities, the ranking of their value per ton of wood consumed does not change.

This comparison suggests that, from a global economic standpoint, it would always make better economic sense to capture products from wood from highest value to lowest, i.e. to use high quality bole wood first for lumber or other solid wood products. The residue from lumber production should be used to produce fiber. Any remaining residues from lumber manufacture or pulping should be converted to liquid fuels such as ethanol, and then to electrical power. Please note that this is not a new philosophical argument. It has been the practice of the Forest Products Industry for well over a century.

#### Cellulosic Biorefineries Worldwide

A number of cellulosic biofuel installations are being constructed or planned around the world, but no production-scale facilities are operating yet. In the U.S., thirteen companies have received U.S. Department of Energy backing to install cellulosic biofuel plants. Their locations are shown in Table 4. Six of these plants will use forest biomass as feedstock. Two of them, New Page and Flambeau River, both in Wisconsin, will produce both fiber and biofuels.

A partnership between two leading U.S. companies in energy (Chevron Corporation) and forest products (Weyerhaeuser Company), announced in early 2008, promises to lead to major biofuels production capability. The new company, Catchlight Energy LLC was created to develop and demonstrate novel technologies for converting cellulose and lignin from a variety of sources into biofuels. Weyerhaeuser Company plans to use its forestland to co-produce energy crops and trees, thus supplying biomass feedstock. Chevron brings the capability for commercialization of those technologies and operation of the resulting biofuels production plants.

Two major biorefinery efforts are under way in Finland. UPM-Kymmene one of the world’s largest pulp and paper manufacturing companies, announced that they will invest in biodiesel plants, which will be built in connection with some of their pulp and paper mills. Their biodiesel technology will be based on Finnish syngas technology, where wood biomass is gasified and then syngas is converted to biodiesel.
Table 4, Locations of biofuels plants in progress in the U.S., supported in part by the U.S. Department of Energy.

**Thermochemical Conversion**
- Range Fuels, Inc., Soperton, GA
- Lignol (KS)
- Flambeau River (WI)
- NewPage (WI)

**Biochemical Conversion**
- Abengoa Bioenergy, Southwestern KS
- BlueFire Ethanol, Inc., Corona, CA
- Poet, Emmetsburg, IA
- Mascoma (MI)
- RSE (ME)
- Pacific Ethanol (OR)
- ICM (MO)
- Altech (KY)
- Verenium (LA)

NSE Biofuels Oy Ltd. will build a demonstration plant in Varkaus, Finland, to develop processes to produce renewable biofuels from wood residues. NSE Biofuels Oy Ltd. is a joint venture between Stora Enso Oyj and Neste Oil Corporation.

In Sweden, SunPine AB is building a production plant in Piteå, Sweden to convert crude tall oil (CTO) either to “crude tall diesel” for subsequent hydrotreatment at a refinery into a renewable diesel component or, via purification, into standard EN14214 biodiesel. The plant will have a capacity of up to 100,000 m³ (26 million gal) of crude tall diesel per year. Construction began in September, 2008 and production is scheduled to begin in September, 2009.

Also in Sweden, CHEMREC AB continues development of its pressurized black liquor gasification technology, with expectations to produce clean syngas for production of biofuels.

**Renewable Fuels: How the Forest and Forest Products Industry Can Contribute and Benefit**

The Forest Products Industry can contribute to and benefit from the growth of a renewable fuels industry in several ways. An important first task is to improve the efficiency of biomass utilization in existing pulp and paper mills. Efficiency improvements include improving biomass conversion efficiency in recovery boilers and hog fuel boilers. It may include reducing steam demand at all pressure levels, for example by reducing soot blowing steam requirements in recovery boilers or low and medium pressure steam demand in evaporators through better water management in pulp mills. Major, capital intensive improvements may be required, from upgrading to high solids concentrators for black liquor to installing integrated combined-cycle power plants for hog fuel or black liquor. To be successful in an integrated biorefinery where liquid fuels and/or power are co-products, the entire complex must be very efficient with regard to energy management and conservation. Finland has a significant advantage in this area, marketing high efficiency recovery boilers, and having led the way to highly energy efficient kraft pulp mills.

The second task is to identify opportunities to integrate fuels or energy production with fiber production. This is illustrated in Figures 2 and 3. Figure 2 shows how energy flows between the three major components of a pulp and paper complex. Wood is the feedstock for both fiber and energy production. Energy is produced from black liquor, bark, and forest residues (lumped here with wood or with residual biomass). The Combined Heat and Power (CHP) plant utilizes these fuels to produce power for internal use and export, and steam to meet process demands.

The diagram in Figure 3 illustrates an integrated forest biorefinery that includes a biofuels plant as well as a pulp and paper mill and a CHP plant. The main difference between the diagrams in Figures 2 and 3 is that, in Figure 3, some or all of the residual biomass from the pulp mill is converted to biofuels in the fuels synthesis plant in Figure 3 before it reaches the CHP plant. More biomass
(wood) input is likely required when both fiber and biofuels are produced.

A third task is to utilize forestlands more effectively to produce biomass for biorefinery feedstock. One possibility is to collect more of the forest residues as feedstock, and to deliver them in a cost-effective way to the biorefinery. A second approach is to utilize forestlands to grow trees and energy crops simultaneously, as is being undertaken by Weyerhaeuser Company in their collaboration with Chevron Corporation.

**Energy and Economic Comparisons for Alternative Forest Biorefineries**

Let us now compare the energy requirements and energy output as products from two different types of biorefineries with those from conventional kraft pulp mills.

**Integrated Ethanol Plant**

In the first case, we compare an integrated biorefinery that consists of a kraft pulp mill and integrated ethanol plant with a stand-alone pulp mill [17]. The pulp production is the same from both plants, but they produce different quantities of power, and consume different amounts of biomass and other energy supplies. The integrated biorefinery produces ethanol from sugars extracted from wood prior to pulping, fiber, and power.

In this example, integration between the ethanol plant and pulp mill includes a common CHP plant that provides steam to both plants, and utilization of residual organic from the ethanol plant as fuel in the CHP plant. The pulp mill has a conventional Tomlinson recovery boiler and steam turbine for power generation, with process steam extraction at three pressures. The CHP plant consists of the recovery boiler, a hog fuel boiler that burns biomass residues from the pulp mill and ethanol plant, and the steam turbines. The process steam production is balanced with the total demand from the integrated biorefinery. To balance the steam demand and production, either unneeded biomass residue from the integrated complex is exported as biofuel or additional fuel (biomass residue) is purchased.

A block diagram representing the stand-alone pulp mill is shown in Figure 4. The energy value of each input and output stream, in millions of Btu/hr, is indicated next to each process stream. This particular mill produces 1398 t/d of fiber with an energy value of 737 million Btu/hr. It also generates a net of 19.3 MW (66 million Btu/hr) of exportable electrical power.

An integrated biorefinery that produces ethanol as well as fiber and power is shown in Figure 5. The fiber production rate is exactly the same as in Figure 4, but the input rates of wood, hog fuel, and natural gas have increased. The energy values...
Figure 4. A block diagram representing energy inputs and outputs to/from a kraft pulp mill. The energy inputs and outputs are indicated next to each process stream.

Figure 5. A block diagram representing an integrated forest biorefinery that produces ethanol and power as well as cellulose fiber.

Table 5. Energy balances and incremental efficiency for fuel and power generation for a biorefinery that consists of an ethanol plant integrated with a kraft pulp mill.

<table>
<thead>
<tr>
<th>Products</th>
<th>Fiber &amp; power</th>
<th>Fiber, ethanol &amp; power</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inputs:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood</td>
<td>2430</td>
<td>3114</td>
</tr>
<tr>
<td>Hog fuel</td>
<td>28</td>
<td>82</td>
</tr>
<tr>
<td>Nat'l gas</td>
<td>121</td>
<td>133</td>
</tr>
<tr>
<td>Power</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>2579</td>
<td>3329</td>
</tr>
<tr>
<td>Difference</td>
<td></td>
<td>750</td>
</tr>
<tr>
<td><strong>Outputs:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fiber</td>
<td>737</td>
<td>737</td>
</tr>
<tr>
<td>Co-products</td>
<td>118</td>
<td>146</td>
</tr>
<tr>
<td>Power</td>
<td>66</td>
<td>269</td>
</tr>
<tr>
<td>Ethanol</td>
<td></td>
<td>173</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy losses</td>
<td>1658</td>
<td>2004</td>
</tr>
<tr>
<td>Total</td>
<td>2579</td>
<td>3329</td>
</tr>
<tr>
<td>Total energy products</td>
<td>66</td>
<td>442</td>
</tr>
<tr>
<td>Difference</td>
<td></td>
<td>376</td>
</tr>
</tbody>
</table>

Incremental efficiency\(^a\) 50%

\(^a\)Incremental increase in energy in products per incremental increase in energy inputs.
of two of the output streams – ethanol and power – account for a significant part of the increase in total energy input.

Table 5 contains an overall energy balance for the examples in Figures 4 and 5. The high energy-value output streams in Figure 5 have a combined energy value of 442 million Btu/hr, nearly 7 times the energy value of net power generated by the pulp mill in Figure 4. This additional energy output is less than the increase in energy input in Figure 5 versus Figure 4. The incremental energy efficiency for ethanol production plus the increase in power generated (Figure 5) is a respectable 50%. By comparison, the efficiency for estimates for stand-alone, ethanol-from-wood plants are from 32% to 41% depending on the efficiency of conversion of wood carbohydrates to fermentable sugars.[12] The gains in energy efficiency come from mass and energy integration within the biorefinery versus a stand-alone ethanol plant. Please see Frederick et al., 2008[12] for details of this case study.

Integrated F-T Hydrocarbons Plant with Upgraded Power Island
The second example is one of an integrated biorefinery that produces hydrocarbons (gasoline precursors) via Fischer-Tropsch (F-T) synthesis from synthesis gas (CO and H₂) as well as producing fiber and power. The analyses presented here is based on a study by Larson et al. [13,14]. The biorefinery in this example actually includes three different options for co-production of fiber, fuel, and power. A major modification for these integrated biorefinery options (but not the stand-alone pulp mill) would be to modify the chemical recovery and power island in the pulp mill to make it more efficient in high-level energy conversion. The most important differences are (a) the Tomlinson recovery boiler is replaced with a high temperature black liquor gasifier that produces synthesis gas at elevated pressure for liquid hydrocarbon production; (b) the hog fuel boiler is replaced with a pressurized fluidized bed gasifier that produces synthesis gas for either power generation (in options A and B), or for conversion to liquid hydrocarbons (in option C); and (c) a gas-fired power turbine is added to generate power from part of the synthesis gas from the biomass gasifier and/or unconverted syngas from the fuel synthesis generate power. In cases B and C, a heat recovery boiler and condensing turbine was used downstream of the gas turbine to produce additional power. Process steam is generated by cooling the hot syngas and by recovering heat from the exothermic reactions in the hydrocarbon synthesis reactors. The process steam production in all options is balanced with the total demand from the integrated biorefinery, with biomass purchased to balance the fuel requirement. Process flow diagrams for each option have been published and are reproduced in Appendix 1 of this document for convenience.

*Table 6, Energy balances and incremental efficiency for fuel and power generation for a biorefinery that consists of a Fischer-Tropsch liquid hydrocarbons plant integrated with a kraft pulp mill.*

<table>
<thead>
<tr>
<th>Energy Inputs (MW)</th>
<th>Base</th>
<th>FTa</th>
<th>FTb</th>
<th>FTc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>723</td>
<td>675</td>
<td>675</td>
<td>675</td>
</tr>
<tr>
<td>Hog fuel</td>
<td>71.4</td>
<td>66.8</td>
<td>66.8</td>
<td>66.8</td>
</tr>
<tr>
<td>Pulp wood residues</td>
<td>0.0</td>
<td>125.4</td>
<td>454.9</td>
<td>557.2</td>
</tr>
<tr>
<td>Lime kiln fuel oil</td>
<td>32.7</td>
<td>37.8</td>
<td>37.8</td>
<td>37.8</td>
</tr>
<tr>
<td>Total</td>
<td>827</td>
<td>905</td>
<td>1235</td>
<td>1337</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Energy Outputs (MW)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber</td>
<td>315.8</td>
<td>315.8</td>
<td>315.8</td>
<td>315.8</td>
</tr>
<tr>
<td>Liquid fuel</td>
<td>0</td>
<td>111.6</td>
<td>111.6</td>
<td>342.7</td>
</tr>
<tr>
<td>Power</td>
<td>64.3</td>
<td>87.7</td>
<td>228.9</td>
<td>77.3</td>
</tr>
<tr>
<td>Total</td>
<td>380.1</td>
<td>515.1</td>
<td>656.3</td>
<td>735.8</td>
</tr>
</tbody>
</table>

Incremental efficiency* 172% 68% 70%
In all options, the fiber production is exactly the same in the stand-alone pulp mill and each biorefinery option, but the energy input as purchased wood residues has increased substantially, as shown in Table 6.

Also shown in Table 6 is the liquid hydrocarbon and power production for each of the three biorefinery configurations. In all three biorefinery cases, there is substantial liquid fuel production and increase in power production.

In biorefinery option A, the heat and power plant is configured to produce liquid hydrocarbons from syngas generated from black liquor only. Single-pass conversion of syngas to liquid fuel is well below 100%, so unconverted syngas from the fuel synthesis reactor is burned in the gas turbine to produce power. Syngas from the biomass gasifier is burned to produce power and is not used for liquid fuel production in this option. In this option, liquid fuel production is nearly 112 MWth, and power generation is increased by 36% beyond the stand-alone pulp mill option.

The design of biorefinery option B is optimized for power production. The input of biomass fuel is increased beyond the minimum required to satisfy pulp mill steam demand, and the syngas produced in the biomass gasifier, along with the unconverted syngas from the fuel synthesis reactor, is used entirely for power and process steam production. In option B, power generation is increased by 256% when compared with the pulp mill base option.

The design of biorefinery option C is optimized for liquid fuel production. Again, the input of biomass fuel is increased, but the syngas produced in the biomass gasifier is used entirely for liquid fuel production. The unconverted syngas from the fuel synthesis reactor is used for power production. In this option, the liquid fuel production is increased by 207% over the other two biorefinery options, while power generation is increased by 20% when compared with the pulp mill base case.

Table 6 also shows the incremental conversion efficiency for the additional biomass purchased for each of the three biorefinery options. In case A, the conversion efficiency is 172%. This surprisingly high incremental efficiency is mainly the result of far more efficient energy conversion by using (a) gasification instead of combustion to convert biomass and black liquor to syngas intermediate, and (b) using a gas combustion turbine rather than a steam power cycle for electrical power production. The incremental efficiencies are also very high for options B and C, 68% and 70% respectively. Please see the references by Larson et al.[13,14] for full details of this case study.

**Capital Investment**

In all of the options considered here, it is assumed that there is an existing kraft pulp mill in good operating condition. The capital costs required to convert the pulp mill to a forest biorefinery are for new equipment for an ethanol plant or F-T hydrocarbons synthesis plant, modification and/or expansion of the chemical recovery and power island as required for each specific case, and modifications to accommodate additional biomass handling, energy integration, etc. Table 7 includes the total incremental capital investment for each case and option considered here. More detailed capital cost summaries are available from Larson et al.[13] and Frederick et al.[12]

The results in Table 7 show that a significant capital investment is required to create a forest biorefinery by integrating a fuel production plant with a kraft pulp mill. The capital investments are not at all unreasonable, however. The capital intensity for a fuel grade ethanol plant with cellulosic feedstock falls in the range of $1.50 to $2.50/MWth depending upon feedstock and plant size [15,16,17].

<table>
<thead>
<tr>
<th>Case &amp; Option</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FT-A</td>
</tr>
<tr>
<td>Total capital</td>
<td>10^6 $</td>
</tr>
<tr>
<td>Fuel production</td>
<td>MW_{th}</td>
</tr>
<tr>
<td>Incremental power Production</td>
<td>MW_{e}</td>
</tr>
<tr>
<td>Capital investment per MW fuel + power</td>
<td>10^6$/MW</td>
</tr>
</tbody>
</table>
**Profitability**

Larson and co-workers estimated that without subsidies, F-T hydrocarbon plants would have a discounted cash flow rate of return (DCFRR) between 14% and 18% on invested capital. With expected subsidies, the DCFRR would increase to between 28% and 34%. In their study, Larson et al.\[13,14\] considered these subsidies: an excise tax credit (currently available for ethanol), an investment tax credit for gasification investments as mandated by EPAct 2005, a 10-year production tax credit for renewable electricity of $9 per MWh, and a renewable energy credit (REC) of $20/MWh.

Co-production of ethanol and fiber from southern pine, the case study summarized here, would not currently be profitable because of loss of cellulose to black liquor from pulping of wood chips from which hemicellulose had been pre-extracted with H\(_2\)SO\(_4\). For at least some other wood species, cellulose is not degraded by dilute acid pre-extraction. In those cases, integrated biorefineries are profitable.

**Summary**

Integrated forest biorefineries that produce transportation fuels and power as well as cellulose fiber are moving closer to becoming real options. Development of at least two of these biorefineries is currently being funded by the U.S. Department of Energy’s Office of Energy Efficiency and Renewable Energy, and several others are under development around the world. An analysis of several published case studies suggests that integrated forest biorefineries would be economically viable, with capital investments in the order of $280 - $500 million required for constructing and integrating fuel and power plants of viable capacity with existing, fully operational kraft pulp mills.
References


Appendix Process flow diagrams for three options for co-producing F-T Hydrocarbons in an integrated biorefinery [13].

Process flowsheet for Option A: biomass gasifier, gas turbine, no syngas recycle.

Process flowsheet for Option B: biomass gasifier, larger gas turbine, no syngas recycle.

Process flowsheet for Option C: syngas from biomass gasifier to fuel synthesis, gas turbine.
Abstract

The composition of carryover particles is of great importance in determining the ability of the particles to deposit on recovery boiler superheater tube surfaces. Results of laboratory and field studies show that chloride (Cl) and potassium (K) contents in carryover particles are linearly proportional to, but much lower than their values in the black liquor. Cl and K enrichment factors for carryover are below 1 and decrease further as the particle temperature increases. Carryover contains more sulphate and less carbonate than smelt. The sulphate content in carryover increases only slightly with an increase in exposure time, suggesting that the majority of sulphate must have formed prior to deposition. There is a linear correlation between Cl and K enrichment factors for the as-fired black liquor, carryover, precipitator ash and smelt. The correlation can be theoretically verified.

Introduction

As black liquor is sprayed and burned in recovery boilers, a small portion of black liquor droplets are entrained in the flue gas where they undergo drying, swelling, devolatizing and char burning, and ultimately, form carryover particles. Due to their relatively large particle size, 100 μm to 3 mm, and high temperatures, carryover particles tend to strike and deposit on tube surfaces in the superheater region of the boiler. The ability of carryover particles to form deposits depends greatly on the liquid content of the particles at the moment of impact, which, in turn, is a function of particle temperature and composition, mainly the chloride (Cl), potassium (K) and sulphide (S) contents [1-3].

Since the composition of carryover continuously changes during combustion, it varies greatly from boiler to boiler, and from location to location in a given boiler, depending on particle residence time, liquor composition, solids content and droplet size, flue gas temperature and burning conditions in the lower furnace. As a result, the composition is usually not known, particularly at the moment immediately before the particles strike the tube surface. This makes it difficult to determine the fouling tendency of the particles, i.e. whether the particles would deposit on the tube surface upon impact.

Much work has been done over the past decade to systematically study the composition of carryover particles under controlled environment using an Entrained Flow Reactor (EFR) and to examine important parameters that affect the composition [3,4]. Field studies were also performed using air-cooled probes to collect carryover samples in the superheater region of recovery boilers, and to examine how the composition is affected by liquor composition and boiler operation [5,6]. This paper summarizes the key findings obtained from these studies and discusses their practical implications for recovery boiler operation.

Laboratory Studies

Six black liquor samples from five different kraft pulp mills were used either as-is or were mixed with various amounts of precipitator dust collected from the same recovery boiler as the black liquor, or were mixed with various amounts of pure KCl to obtain a wide range of Cl and K contents [4]. The mixed black liquor samples were poured onto stainless steel trays to form a thin sheet, which was dried in an oven controlled at 130°C, and were then ground and sieved to make dried particles in the size range of 300-500 μm. The dried particles were fed into the EFR which was set at 800°C. A mixture of natural gas combustion products with a varying amount of excess air flowed through the EFR with a velocity of 1.8
m/s. Four different O2 concentrations were used, 1.7, 6.2, 9.5, and 12.3%.

Carryover particles collected at the EFR exit were analyzed for residual char, sodium (Na), potassium (K), chloride (Cl), sulphide (S), sulphate (SO4), and carbonate (CO3) contents. The composition was expressed in mole% Cl/(Na+K) for Cl, mole% K/(Na+K) for K, mole% CO3/(Na2+K2) for carbonate, mole% SO4/(Na2+K2) for sulphate, and mole% S/(Na2+K2) for sulphide. The total sulphur content was expressed as mole% S total /(Na2+K2) in carryover and that in black liquor at various O2 concentrations.

Figure 2. Correlation between chloride content in carryover and that in black liquor at various O2 concentrations.

Figure 3. Correlation between potassium content in carryover and that in black liquor at various O2 concentrations.

Cl and K Contents
As shown in Figure 1, at a given O2 concentration, the chloride content in carryover increased linearly with an increase in chloride content in the black liquor. For a given black liquor sample, however, burning at a higher O2 concentration resulted in carryover that had a lower Cl content. The results are plausible since a higher O2 concentration would give rise to a higher particle temperature, and hence a greater amount of Cl and K vaporized from the particles.

The enrichment factors for chloride (EFCl) and potassium (EFK) are typically defined respectively as the ratios of the mole fractions of Cl and K in carryover to the mole fractions of Cl and K in the black liquor. Thus, the slope of each line in Figure 1 is essentially the same as the Cl enrichment factor (EFCl) in carryover at each O2 concentration. At 1.7%O2, for instance, the slope is 0.78 or EFCl = 0.78; the chloride content in carryover was about 78% of that in black liquor. At 12.3%O2, the slope is much lower, 0.3 or EFCl = 0.3; the chloride content in carryover was only 30% of that in black liquor.

Similarly, the slope of each line in Figure 2 is the same as the K enrichment factor (EFK) in carryover at each O2 concentration. In this case, however, the decrease in K content in carryover was much less than the decrease in Cl content (i.e. the data are located closer to the diagonal line in Figure 2 than they are in Figure 1). This implies that the enrichment factor for K in carryover is much higher than that for Cl.

Figure 3 shows a clear linear relationship with a R^2 value of 0.998 between EFK and EFCl values for all four O2 concentrations tested in this study. Extrapolating the line on both ends (broken lines) shows that when EFCl = 1, EFK = 1 and when EFCl = 0, EFK = 0.68. These two end points suggest that if Cl is not deleted at all from the carryover, then potassium is not deleted either. On the other hand, if Cl is completely deleted from the carryover (0% Cl), there is still 68% K left in the carryover compared to that in the black liquor. The linear correlation between EFCl and EFK is intriguing, but it can be theoretically explained as will be seen later in this paper.
**CO₃, SO₄, S and S_total Contents**

Figure 4 shows the change in carbonate, sulphate, sulphide and total sulphur contents in carryover produced from the same black liquor at different O₂ concentrations. The sulphide content decreased from 5 mole% S/(Na⁺+K⁺) at 1.5% O₂ to zero at 12.5% O₂ due to oxidation to sulphate. The sulphate content increased from 15 mole% SO₄/(Na⁺+K⁺) at 1.5% O₂ to 40 mole% SO₄/(Na⁺+K⁺) at 12.5% O₂, which is much more than the decrease in sulphide content. The carbonate content decreased from 75 to 55 mole% CO₃/(Na⁺+K⁺). The extent of decrease in carbonate content is essentially the same as that of the total increase in total sulfur content. These results are consistent with the fact that black liquor burning at a higher temperature would retain more sulphur in the char/smelte residue, and would release less S to the gas in the form of SO₂.

Since the retention time of the particles in the EFR was less than 2 seconds, the above results imply that the formation of sulphate in carryover in an oxidizing environment is a rapid process that occurred during combustion, and not a result of the sulphation of carbonate after the carryover has been formed.

**Effect of Gas Temperature**

The effect of gas temperature on Cl and K contents in carryover was studied on two black liquor samples of different Cl and K compositions. Sample #1 contained low Cl and high K, while Sample #2 contained high Cl and low K. The gas temperature was changed by operating the EFR at different temperatures.

As expected, Cl and K contents in both carryover samples decreased with an increase in gas temperature (Figure 5). The sulphate content in both carryover samples, however, increased with an increase in gas temperature. This again confirms the results shown in Figure 4 that carryover formed at higher temperatures retains more sulphur.

**Field Studies**

In order to examine if the above laboratory results using the EFR were applicable to conditions in recovery boilers, field studies were performed on three operating boilers. Boiler A was the only recovery boiler at a kraft mill in Eastern Canada. Boilers B and C were two of the three recovery boilers at a kraft mill in Southern United States, burning black liquor of a similar composition.
Carryover Collecting Probe
The probe consists of two concentric stainless steel pipes. The outer pipe is 50 mm in ID and 3 m long. The inner pipe, 25 mm in ID and 3.2 mm long, is equipped with a removable carryover sampling tip, a thermocouple embedded on the pipe surface near the tip, and a cooling system that regulates the compressed air flow through the inner probe to keep the sampling tip at a desired temperature. The outer pipe acts as a shield to prevent fume from condensing on the surface of the sampling tip. A small tube is inserted through the inner pipe to collect flue gas samples from the boiler using a vacuum pump.

Figure 6. Air-cooled sampling probe used for collecting carryover particles from operating boilers.

The probe was inserted 1.5 to 2 m into each boiler through an opening ahead of the superheater at the bull nose elevation. The carryover sampling tip of the inner pipe was kept inside the outer shield pipe when the probe was first inserted in the boiler. As the sampling tip temperature reached about 500°C, it was pushed out of the shield pipe to be exposed to the flue gas. This procedure was necessary in order to prevent condensed fume from depositing on the sampling tip while it was still “cold” at the start of the test. The probe was exposed in the boiler for different time intervals to examine how carryover composition may change with time. At the end of each test, the sampling tip was pulled back into the outer shield pipe before the entire probe was retracted from the boiler. As the probe had been sufficiently cooled down, the sampling tip, along with the carryover sample on its surface, was removed from the inner pipe tube, and wrapped and stored in a shielded plastic bag. A new or clean sampling tip was used for the next test.

At about the same time as carryover sampling, samples of as-fired black liquor, smelt, and precipitator dust of each boiler were also collected and analyzed.

Table 1 summarizes Na, K, and Cl contents in the as-fired black liquors of the boilers. Boilers B and C had a similar black liquor composition, reflecting the fact that they are in the same mill. Boiler A had a lower Cl content and a higher K content compared to Boilers B and C. These as-fired black liquor concentrations were used in the calculation of Cl and K enrichment factors in the carryover, smelt and precipitator dust samples.

Table 1. As-fired Black Liquor and Flue Gas Analyses at the Sampling Locations

<table>
<thead>
<tr>
<th></th>
<th>BOILER</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As-fired BL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na, wt% d.s.</td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td></td>
<td>18.1</td>
<td>19.3</td>
<td>20.0</td>
</tr>
<tr>
<td>K, wt% d.s.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.7</td>
<td>2.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Cl, wt% d.s.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>mole% Cl/(Na+K)</td>
<td>1.9</td>
<td>3.5</td>
<td>3.1</td>
</tr>
<tr>
<td>mole% K/(Na+K)</td>
<td>10.7</td>
<td>5.8</td>
<td>5.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flue Gas</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>900 ± 20</td>
<td>863 ± 20</td>
<td>815±15</td>
</tr>
<tr>
<td>Excess O₂, %</td>
<td>2.2</td>
<td>2.2</td>
<td>2.0</td>
</tr>
<tr>
<td>SO₂, ppm</td>
<td>N/A</td>
<td>20</td>
<td>30</td>
</tr>
</tbody>
</table>

The temperature and O₂ and SO₂ concentrations in the flue gas at the sampling locations. The flue gas temperature in Boiler A was the highest, followed by Boiler B and Boiler C. Excess O₂ and SO₂ concentrations were similar in all three boilers.

Enrichment Factors of Cl and K
Figure 7 shows the enrichment factors for Cl and K in carryover deposits collected from boilers A, B, and C, along with those for smelt (shown at time = 0). In all cases, the enrichment factors were less than 1, indicating that both carryover deposits and smelt in each boiler contained less Cl and K than the as-fired black liquor of the boiler. The average EF₁ Cl value was about 0.8 for smelt, and significantly lower (about 0.5) for carryover deposits. In each boiler, no significant difference in EF₁ Cl value was observed between carryover deposits from different sampling times, except for the 12-minute sample from Boiler B, which showed a significantly higher EF₁ Cl value than other samples. This outlier (noted with an asterisk (*)) in the Figure was due probably to the contamination of the sample by fume deposits which usually contain much more Cl and K than carryover deposits.

Similar results were obtained for potassium, although the average EF₁ K value was higher than the average EF₁ Cl value (Figure 8). It was close to 1 for smelt, but varied between 0.8 and 0.9 for carryover deposits.
The higher EF\textsubscript{K} value compared to EF\textsubscript{Cl} value is due to the fact that potassium compounds are not only in the form of KCl, but also K\textsubscript{2}SO\textsubscript{4}, K\textsubscript{2}S and K\textsubscript{2}CO\textsubscript{3}, whereas chloride compounds can only be in the form of NaCl and KCl, which are much more volatile than other alkali compounds.

Extrapolating the carryover sample data to zero sampling time in Figures 7 and 8 respectively gives EF\textsubscript{Cl} and EF\textsubscript{K} values of about 0.5 and 0.8 for “freshly formed” carryover. These values are significantly lower than those for smelt. This is plausible since carryover particles were exposed to a more oxidizing atmosphere and a higher temperature than smelt in the lower furnace. High temperatures cause more NaCl and KCl to vaporize and thus more Cl and K to be lost from the particles. The results are consistent with the data obtained using EFR (Figures 3 and 5).

Figure 9 shows the average EF\textsubscript{K} values plotted against the average EF\textsubscript{Cl} values for all types of samples taken from boilers A, B, and C. By definition, as-fired black liquor samples have an enrichment factor of 1. Carryover deposits and smelt samples have enrichment factors of less than 1, while precipitator ash samples, which are significantly enriched in Cl and K, have enrichment factors of much greater than 1. The correlation between EF\textsubscript{K} and EF\textsubscript{Cl} of these samples for boilers A and B appears to be linear. These results are consistent with those reported by Janka et al [6].

For Boiler C, the data point for the precipitator ash did not fall on to the same line as the data points for carryover, smelt and black liquor (broken line). The expected linear relationship implies the measured EF\textsubscript{Cl} and EF\textsubscript{K} values for Boiler C.
precipitator ash must have been wrong. Either the EF_{Cl} value should have been higher or the EF_{K} value measured K content been lower, or both.

CO_3, SO_4 and S Contents

In order to enable a comparison between carryover composition and smelt composition, mole% CO_3/(Na_2+K_2) was used for carbonate, mole% SO_4/(Na_2+K_2) for sulphate and mole% S/(Na_2+K_2) for sulphide.

Figure 10 shows the total sulphate, expressed as mole% (S+SO_4)/(Na_2+K_2) and carbonate contents of carryover samples from Boilers A, B, and C, along with the composition of oxidized smelt (shown in these figures at time = 0), which was taken to be the composition of smelt with all sulphide converted to sulphate. The carryover deposits contained more total sulphate and less carbonate than oxidized smelt. For carryover samples collected over short exposure times, the total sulphate content increased slightly while the carbonate content decreased with sampling time. These results suggest that although some sulphation of the carbonate in carryover may have occurred on the probe, the majority of the sulphation must have occurred during black liquor combustion, before deposition.

Note also from Figure 10 that while the total sulphate and carbonate contents of oxidized smelt in Boilers B and C were similar (since these boilers were burning the same black liquor at the same pulp mill), the total sulphate content of carryover in Boiler C was significantly higher than in Boiler B. This, together with the higher carbonate content of Boiler C precipitator dust, suggests that Boiler C may have been operated at a higher temperature in the lower furnace than Boiler B. Higher temperatures minimize sulphur release and thus help keep the sulphur in carryover.

Theoretical Consideration

The apparent linear relationship obtained in this study between Cl and K enrichment factors for the as-fired black liquor, carryover, precipitator ash and smelt (Figure 9) and that obtained by Janka et al [6] for different boilers at different mills is intriguing. It suggests that there is a good reason for such a linear correlation to exist. It is, therefore, worthwhile to examine if such a correlation can be theoretically verified.

Consider a system involving three streams, in which either stream 1 mixes with stream 2 to form stream 3, or stream 3 splits into stream 2 and stream 1, as shown in Figure 11.

Figure 10. Total sulphate and carbonate content of the oxidized smelt and carryover deposit from boilers A, B and C (oxidized smelt shown at time = 0).
Figure 11. System with three streams

F₁, F₂, and F₃ are respectively the mass flows of stream 1, stream 2, and stream 3.

\[ F_1 + F_2 = F_3 \]  \hspace{1cm} (1)

If “a” and “b” are two species in 1, stream 2, and stream 3, then

\[ F_1 C_{a1} + F_2 C_{a2} = F_3 C_{a3} \]  \hspace{1cm} (2)

\[ F_1 C_{b1} + F_2 C_{b2} = F_3 C_{b3} \]  \hspace{1cm} (3)

where \( C_{a1}, C_{a2}, \) and \( C_{a3} \) are concentrations, in wt%, of “a” in streams 1, 2, and 3, respectively; and \( C_{b1}, C_{b2}, \) and \( C_{b3} \) are concentrations, in wt%, of “b” in streams 1, 2, and 3, respectively.

Rearrange (3) gives:

\[ C_{b2} = \frac{F_1 C_{b3} - F_1 C_{b1}}{F_2} \]  \hspace{1cm} (4)

\[ C_{b2} - C_{b1} = \frac{F_1 C_{b3} - F_1 C_{b1} - F_2 C_{b1}}{F_2} \]

Hence

\[ C_{b2} - C_{b1} = \frac{F_1 (C_{b3} - C_{b1})}{F_2} \]  \hspace{1cm} (5)

Similarly

\[ C_{a2} - C_{a1} = \frac{F_1 (C_{a3} - C_{a1})}{F_2} \]  \hspace{1cm} (6)

\[ C_{b2} - C_{b3} = \frac{F_1 (C_{b3} - C_{b1})}{F_2} \]  \hspace{1cm} (7)

Equations (9) and (10) give:

\[ \frac{C_{b2} - C_{b1}}{C_{a2} - C_{a1}} = \frac{C_{b3} - C_{b1}}{C_{a3} - C_{a1}} \]  \hspace{1cm} (9)

\[ \frac{C_{b2} - C_{b3}}{C_{a2} - C_{a1}} = \frac{C_{b2} - C_{b3}}{C_{a2} - C_{a3}} \]  \hspace{1cm} (10)

Equation (11) indicates that the wt% concentration of “b” in streams 1, 2 and 3 is linearly proportional to that of “a”, as schematically shown in Figure 12.

Virgin Black Liquor, As-fired Black Liquor and Precipitator Dust

Consider a case around a recovery boiler (Figure 13), where \( F_{VBL}, F_{AFBL}, F_{Smelt}, \) and \( F_{Stack} \) respectively represent the mass flows of virgin black liquor, precipitator dust, as-fired black liquor, smelt, and stack gas.
From the material balance around the mix tank:
\[ F_{Vg\,BL} + F_{Dust} = F_{AF\,BL} \]  \hspace{1cm} (12)

Applying (11) to these three streams for Cl and K yields:
\[ \frac{C_{Cl(Dust)} - C_{Cl(Vg\,BL)}}{C_{K(Dust)} - C_{K(Vg\,BL)}} = \frac{C_{Cl(Dust)} - C_{Cl(AF\,BL)}}{C_{K(Dust)} - C_{K(AF\,BL)}} \]  \hspace{1cm} (13)

Equation (13) means that the weight concentrations of Cl in precipitator dust, virgin black liquor and as-fired black liquor are linearly proportional to the weight concentrations of K, as shown in Figure 13. Flow around a Recovery Boiler

Figure 13. Flow around a Recovery Boiler

Or
\[ \frac{C_{Cl\,mole(Dust)}}{C_{K\,mole(Dust)}} = 1.1 \times \frac{C_{Cl\,mole(AF\,BL)}}{C_{K\,mole(AF\,BL)}} \]  \hspace{1cm} (14)

(13) and (14) give:
\[ \frac{C_{Cl\,mole(Dust)} - C_{Cl\,mole(Vg\,BL)}}{K_{mole(Dust)} - K_{mole(Vg\,BL)}} = \frac{C_{Cl\,mole(Dust)} - C_{Cl\,mole(AF\,BL)}}{K_{mole(Dust)} - K_{mole(AF\,BL)}} \]  \hspace{1cm} (15)

This means that the linear relationship is also held when the Cl and K concentrations are expressed as mole% Cl/(Na+K) and mole% K/(Na+K), as shown in Figure 14.

Figure 14. Linear correlation between wt% Cl and wt% K of virgin black liquor, as-fired black liquor and precipitator dust

If Cl\textsubscript{mole} and K\textsubscript{mole} are the molar concentrations of chloride and potassium, and Cl\textsubscript{wt} and K\textsubscript{wt} are weight concentrations of chloride and potassium, then:

\[ \frac{Cl\textsubscript{mole}}{K\textsubscript{mole}} = \frac{Cl\textsubscript{wt}}{35.5} \left( \frac{Na\textsubscript{wt}}{23} + \frac{K\textsubscript{wt}}{39.1} \right) \]

\[ \frac{Cl\textsubscript{mole}}{K\textsubscript{mole}} = \frac{Cl\textsubscript{wt}}{39.1} \left( \frac{Na\textsubscript{wt}}{23} + \frac{K\textsubscript{wt}}{39.1} \right) \]

Figure 14. Linear correlation between mole% Cl/(Na+K) and mole% K/(Na+K) of virgin black liquor, as-fired black liquor and precipitator dust

Now let EF\textsubscript{Cl} and EF\textsubscript{K} be enrichment factors for Cl and K with respect to as-fired black liquor and rearrange (15), we have:

\[ \frac{Cl\textsubscript{mole(Dust)}}{Cl\textsubscript{mole(AF\,BL)}} - \frac{Cl\textsubscript{mole(Vg\,BL)}}{Cl\textsubscript{mole(AF\,BL)}} = \frac{K\textsubscript{mole(Dust)}}{K\textsubscript{mole(AF\,BL)}} - \frac{K\textsubscript{mole(AF\,BL)}}{K\textsubscript{mole(AF\,BL)}} \]

Or
\[ \frac{EF_{Cl(Dust)} - EF_{Cl(Vg\,BL)}}{EF_{K(Dust)} - EF_{K(Vg\,BL)}} = \frac{EF_{Cl(AF\,BL)}}{EF_{K(AF\,BL)}} \]  \hspace{1cm} (16)

Since EF for as-fired black liquor is equal to 1, (16) becomes
This indicates that the linear relationship will also hold if the Cl and K concentrations in dust, virgin black liquor and as-fired black liquor are expressed as enrichment factors (Figure 16).

\[
\frac{\text{EF}_{\text{Cl(Dust)}} - \text{EF}_{\text{Cl(Vg BL)}}}{\text{EF}_{\text{K(Dust)}} - \text{EF}_{\text{K(Vg BL)}}} = \frac{\text{EF}_{\text{Cl(Dust)}} - 1}{\text{EF}_{\text{K(Dust)}} - 1} \tag{17}
\]

Figure 16. Linear correlation between \(\text{EF}_{\text{Cl}}\) and \(\text{EF}_{\text{K}}\) of virgin black liquor, as-fired black liquor and precipitator dust

Carryover, Fume and Smelt

For carryover, fume and smelt, the material balance around the black liquor mix tank does not apply. The material balance around the recovery boiler (Figure 13) cannot be readily used either, because there are more than three streams involved (i.e. as-fired black liquor, smelt, precipitator dust, and stack gas). A different approach is needed.

Consider an as-fired black liquor particle entrained in the flue gas. As it burns and becomes a carryover particle, some Na, K and Cl in the particle are inevitably lost to the flue gas due to vaporization and chemical reactions, and subsequently condense to form NaCl/KCl fume.

If \(N_{\text{at}}, K_{t}, \text{and } \text{Cl}_{t}\) are respectively the numbers of moles of Na, K and Cl in the initial carryover particle; \(N_{\text{af}}, K_{f}, \text{and } \text{Cl}_{f}\) are respectively the numbers of moles of Na, K and Cl that have been lost to the flue gas and later become fume, and \(N_{\text{at}}, K_{t}, \text{and } \text{Cl}_{t}\) are respectively the numbers of moles of Na, K and Cl that remain in the final carryover particle, then:

\[
N_{\text{at}} = xN_{\text{ai}}, K_{t} = yK_{i}, \text{and } \text{Cl}_{t} = z\text{Cl}_{i}
\]

\[
N_{\text{af}} = (1-x)N_{\text{ai}}, K_{f} = (1-y)K_{i}, \text{and } \text{Cl}_{f} = (1-z)\text{Cl}_{i}
\]

where \(x, y \text{ and } z\) are respectively the mass portions of Na, K, and Cl lost to the flue gas.

\[
\text{EF}_{\text{Cl}} = \frac{\text{Cl}_{t} - \text{Cl}_{i}}{\text{Cl}_{t} - \text{Cl}_{f}}
\]

\[
\text{EF}_{\text{K}} = \frac{K_{t} - K_{i}}{K_{t} - K_{f}}
\]

\[
\text{EF}_{\text{Cl}}(\text{Carryover}) = \frac{\text{Cl}_{f}}{\text{Cl}_{i}}
\]

\[
\text{EF}_{\text{K}}(\text{Carryover}) = \frac{K_{f}}{K_{i}}
\]

\[
\frac{\text{Cl}_{f}}{\text{Cl}_{i}} = \frac{N_{\text{af}}+K_{f}+\text{Cl}_{f}}{N_{\text{at}}+K_{t}+\text{Cl}_{t}}
\]

\[
\frac{K_{f}}{K_{i}} = \frac{N_{\text{af}}+K_{f}+\text{Cl}_{f}}{N_{\text{at}}+K_{t}+\text{Cl}_{t}}
\]

\[
\text{EF}_{\text{Cl}}(\text{Fume}) \approx \frac{\text{Cl}_{f}}{\text{Cl}_{i}} = \frac{N_{\text{af}}+K_{f}+\text{Cl}_{f}}{N_{\text{at}}+K_{t}+\text{Cl}_{t}}
\]

\[
\text{EF}_{\text{K}}(\text{Fume}) \approx \frac{K_{f}}{K_{i}} = \frac{N_{\text{af}}+K_{f}+\text{Cl}_{f}}{N_{\text{at}}+K_{t}+\text{Cl}_{t}}
\]

\[
\text{EF}_{\text{Cl}}(\text{Fume}) \approx \frac{\text{EF}_{\text{Cl}}(\text{Carryover})}{\text{EF}_{\text{Cl}}(\text{Initial})}
\]

\[
\text{EF}_{\text{K}}(\text{Fume}) \approx \frac{\text{EF}_{\text{K}}(\text{Carryover})}{\text{EF}_{\text{K}}(\text{Initial})}
\]

Thus

\[
\text{Cl}_{mole(\text{Fume})} - \text{Cl}_{mole(\text{AF BL})} = \text{Cl}_{mole(\text{Fume})} - \text{Cl}_{mole(\text{Initial})}
\]

\[
\text{K}_{mole(\text{Fume})} - \text{K}_{mole(\text{AF BL})} = \text{K}_{mole(\text{Fume})} - \text{K}_{mole(\text{Initial})}
\]

\[
\text{EF}_{\text{Cl(Fume)}} \approx \frac{1}{\text{EF}_{\text{Cl(Fume)}} - \text{EF}_{\text{Cl(Carryover)}}}
\]

\[
\text{EF}_{\text{K(Fume)}} \approx \frac{1}{\text{EF}_{\text{K(Fume)}} - \text{EF}_{\text{K(Carryover)}}}
\]

Equations (20) and (21) mean that the relationship between the Cl and K concentrations (expressed either as mole% or enrichment factor) in carryover, fume and as-fired black liquor is linear.
dust and Cl lost to stack gas are negligible (as in the case when the precipitator efficiency is high and there are little HCl emissions), the amounts of Na, Cl and K in smelt are equal to those in virgin black liquor.

Based on the relationships between fume and precipitator dust, and between smelt and virgin black liquor, and Equations (17) and (22), it can be concluded that the enrichment factors (or concentrations) of Cl and K in fume, dust, carryover, smelt, virgin black liquor and as-fired black liquor are linearly related, as summarized in Figure 17.

![Figure 17. Linear correlation between EF Cl and EF K of virgin black liquor, as-fired black liquor, carryover, fume and precipitator dust.](image)

**Summary**

A systematic study on carryover composition was performed in the laboratory using an Entrained Flow Reactor (EFR) and on three operating recovery boilers. The results show that carryover particles contain much less Cl and K than the original black liquor. The sulphate (SO₄) content increases with an increase in exposure time and temperature, while the carbonate (CO₃) content decreases. The majority of sulphate in the carryover is formed during combustion, prior to deposition.

The results also show a linear correlation between the amounts of Cl and K in samples of as-fired black liquor, smelt, precipitator dust and carryover deposits. This correlation can be theoretically derived based on Na, K, and Cl balances around the recovery boiler.

**Acknowledgements**

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**References**
