CONTINUOUS DEVELOPMENT OF RECOVERY BOILER TECHNOLOGY – 50 YEARS OF COOPERATION IN FINLAND

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Recovery boiler co-operation in Finland is celebrating its 50th anniversary this year. To celebrate the occasion this anniversary conference is arranged at the 2014 International Chemical Recovery Conference (ICRC) in Tampere, Finland.

Formal co-operation between Finnish recovery boiler users and manufacturers to solve problems of the field was initiated in 1964 with jointly sponsored recovery boiler corrosion study from 1965 to 1968. A few years earlier several mills had experienced severe corrosion in furnace wall tubes which had led to expensive maintenance shutdowns. The first research project was participated by all the Finnish sulphate pulp mills who owned recovery boilers. This research project succeeded so well that the need to co-operate even more closely was recognised and other investigations into various operational and constructional problems were added to the work programme.

Since the beginning, the Finnish Recovery Boiler Committee has been active in promoting safe, economic and environmentally friendly operation of recovery boilers and closely related processes. The strength of recovery boiler co-operation in Finland has always been the open discussion on recovery boiler and related problems between people who have wide-ranging experience and people with in-depth theoretical knowledge. The main emphasis of the FRBC has been put on research, although mutual exchange of experience and distributing knowledge of recovery equipment and operation both at home and abroad has always been an important part in co-operation. Annual recovery boiler day and chief engineer day are important occasions for networking.

Today the FRBC has 23 members which include pulp mills, recovery boiler manufacturers, a number of insurance companies, engineering companies, research organisations and universities in Finland. The FRBC 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 past ten years the FRBC has conducted two large publicly funded research programs. The Finnish Funding Agency for Technology and Innovation (Tekes) was the main financier on both programs. The first program SOTU 2 (2003-2006) concentrated on the possibilities to increase power production from the recovery boilers. Second program SKYREC (2008-2012) developed the studies of SOTU and deepened the understanding needed in the design and operation of the high-efficiency recovery boilers in the future.

Today the future of pulp industry in Finland looks brighter than some years ago and pulp mills are developed towards bioproduct mills with wider product portfolio and higher energy yield. This also puts pressure on chemical recovery and recovery boilers. Therefore, the good research work on this field and co-operation between the members of FRBC is just as important as it was 50 years ago.

It is a great pleasure to welcome you all to this anniversary conference. Learn, network and have fun.
Introduction

Kraft recovery boiler technology has advanced dramatically since the first installations in the late 1930s. The advancement is naturally visible in a number of technological aspects but maybe the most exciting development has dealt with the furnace process. A deeper and more detailed understanding of the recovery boiler furnace process has been one key to a number of major improvements of the technology.

This better understanding is a result of ingenious research efforts by talented people at a number of universities, research centres and industrial laboratories around the world. Today, the archived scientific literature contains around 8000 papers dealing with black liquor. Around 1100 of the papers deal more specifically with black liquor combustion. The interest in black liquor combustion research has steadily increased since the 1980’s. During the last years around 20 new papers have been published per year (Figure 1).

The 50-year anniversary seminar of the Finnish Recovery Boiler Committee at the International Chemical Recovery Conference is an excellent event to summarize some of this great research and development work. This presentation aims at a not-so-serious list of top-10 past research efforts, which have had a significant influence on recovery boiler design or operation. The focus is on research related to liquor combustion and the furnace process.

The top-10 ranking is based on a longer initial list of candidate research topics defined by this author. (There is no reason to hide the fact that the topics selected do quite much reflect the interests of the present author.) These suggested topics were then evaluated and ranked by a panel consisted of four senior recovery boiler experts. The four panel experts represent boiler users, boiler manufacturers and boiler consultants, and their total common experience of recovery boiler technology exceeds one hundred years. Two of the panel experts come from Europe, two from North America.

The panel was asked to comment the suggested research efforts and grade them on a scale from 1 to 5 according to the following: 5 = very significant/interesting/useful, 1 = only marginally interesting. The panel members did their evaluation independently of each other.

This presentation cannot be a comprehensive review of the history and details of all the research topics ranked. Each topic is only briefly

Figure 1. Number of scientific publications dealing with black liquor combustion. Based on the Science Finder by April 2014.
described together with some comments from the evaluation panel. In all cases reference is made to a few literature sources by some of the contributing research groups in the area.

The first five most significant research efforts

Two research topics received full grades from all the four panel members. Interestingly, both were efforts done already several decades ago. Maybe not so surprisingly, they are connected to the two long-term challenges of the recovery boiler technology, corrosion and fouling.

Effort 1 (Shared): Lower furnace wall corrosion

The first one was the “Research in the mechanisms of lower furnace wall corrosion and development of composite tubes – allowing higher boiler pressures (1970s)”. This research was one of the first recovery boiler related research activities done as an organized co-operation project between the boiler users and manufacturers.

The history of this research goes back to the end of the 1960s and 1970s when water/steam pressures of the new recovery boilers were increased for higher electrical efficiency. In these new installations the problem of furnace wall tube corrosion became aggressive. The corrosion was concentrated in the lower furnace and it was clearly connected to the higher tube material temperatures. The Finnish and Swedish Recovery Boiler committees initiated a common research program to study the chemical details of the corrosion and to find solutions to the problem.

The studies included short-term corrosion exposure of a variety of steel qualities in synthetic environments simulating the lower furnace conditions with reduced sulphur gases present (Moberg et al. 1974). Figure 2 summarizes the most important result from these studies. This type of corrosion, sulfidation, steeply increased for all low alloy steels when the material temperature increased above some 280-300 °C. However, with an addition of sufficient amount of chromium in the steel (above some 13%), this corrosion was practically completely inhibited up to temperatures far higher than 400 °C.

Figure 2. Effect of Cr content on corrosion resistance of steels during short term tests at 400 °C in a simulated lower furnace gas (Moberg et al. 1974).

This research paved the road to replacing of the furnace carbon steel tubes with composite tubes. The composite tube consists of two alloys metallurgically bonded together. The outer alloy – Cr containing stainless steel – withstands the fireside corrosion, while the inner – carbon steel - is the ordinary approved pressure vessel material. The first composite tubes were installed in 1972 in Sweden. By 1982 there were already 30 composite tube furnaces in Scandinavia. Today composite tubes are the standard solution in all high-pressure boilers.

As mentioned, the panel members all gave the full five points and had several positive comments:

“A great example of problem-oriented research that finally solved the issues and new compound materials were launched as a result of the project...”

“Vital”

“This was a most important thing. With the composite tubes the furnace corrosion was controlled. This way the reliability and safety could be dramatically improved. When these fundamental things were fixed we could focus on developing other things”

Effort 1 (shared): Dust chemistry and melting

The second effort, which received full grades from all the panel members, was described “Research on dust fouling behaviour and the role of potassium and chloride on dust melting properties (1980-90)”. This research consists of a great number of studies in several research groups, especially at the University of Toronto, Åbo Akademi University, Oregon State University and the Institute of Paper Science and Technology. Most of this advancement took place in the 1980s and early 1990s.

This research has shown how the behaviour of the dust particles and deposits is closely connected to the melting properties of the dust. The complicated phenomenon of partial melting of the dust was described by four characteristic temperatures based on the share of liquid phase at that temperature (Backman et al. 1987, Tran 1997):

- First melting temperature, T₀
- Sticky temperature, Tₛ
- Flow temperature, or radical deformation temperature, Tₘ
- Complete melting temperature, Tₘ₀

These characteristic temperatures are strongly dependent on the dust composition and have a direct connection to the fouling or corrosion properties of the dust in the boiler. The research showed how the characteristic temperatures for a given dust composition could be determined based on phase equilibrium diagrams, or later by using advanced thermodynamic equilibrium calculations. The well-cited Figure 3a shows how the sticky temperature of the fine condensed dust is dependent on the content of chlorine and potassium (Tran 1997). Based on some additional assumptions, the fume sticky temperature could be later related to the Cl and K content in the liquid dry solids directly. Figure 3b shows the same sticky temperature of the dust as function of the Cl and K contents in the black liquor solids.

The panel member comments showed the significance of this work:

“Used every day!”

“Superheater damages and incidents have decreased dramatically since the 1990s. The major reason has been the better understanding of the fly ash behaviour and chemistry...”

“To be able to calculate and predict fly ash behaviour in different parts of the RB helps to design the boilers and optimize heat transfer surfaces more cost-effectively.”

Figure 3. Sticky temperature of the condensed dust (a) as function of the chlorine-to-alkali and potassium-to-alkali ratio in the dust (Tran 1997) (b) as function of Cl and K contents in the black liquor solids (Hupa 2004).

“Very fundamental, today the whole world knows the terms T15 and T70”

Effort 3. Single droplet combustion characterization

The research, “Determining black liquor burning properties (liquor burning stages, swelling tendency) by single droplet tests (1980-90)” was started at Åbo Akademi University and at the Institute of Paper Chemistry in Appleton, Wisconsin (later IPST, Atlanta) in the early 1980s. Black liquor burning behaviour could in an effective way be studied by suspending single liquor droplets on thin Platinum wire and let them burn in a laboratory furnace under controlled conditions. This measuring system appeared to be very suitable for to the relatively large size (several mm) black liquor droplets, which typically require 10-30 seconds to burn...
out. By recording the combustion process four burning stages could clearly be identified and studied:

- Drying
- Pyrolysis and devolatilization
- Char burning
- Inorganic reactions

Figure 4 shows results produced with this technique (Hupa et al. 1987). At the beginning the technique was used to detect differences in the burning properties of different liquors. Especially the characteristic swelling of the burning droplet during the devolatilization stage was shown to vary significantly from liquor to liquor (Frederick et al. 1991). This difference in the swelling tendency was shown to be significant from a practical point of view. At identical conditions the liquors with a heavy swelling tendency were shown to burn faster than the liquors that swell less. The swelling also influences the aerodynamic behaviour of the liquor droplets in the furnace.

The single droplet technique has been thoroughly used to generate experimental information for mathematical descriptions of the droplet burning process (Järvinen 2002). These droplet-burning models have been essential components in all more general furnace process models (Mueller et al. 2004). Later the single droplet technique has been further developed with a variety of analysis techniques to study the fate of sulphur, nitrogen and sodium during the combustion process. The panel members commented this research:

“Introduction of single-droplet furnace was a big step towards the understanding of different stages in BL burning”

“Knowledge about black liquor in-flight burning behaviour from nozzle to char bed is vital to get proper combustion and char bed burning control”

“Fundamental research which also gave a basis for CFD modeling.”

One panel member further suggested additional work on the root-causes of the different burning behaviours (swelling, etc.).

“No, when we are planning to burn lean black liquors, this will be emphasized even more.”

Effort 4. CFD based furnace modelling

“Development of the CFD-based recovery furnace modelling to simulate novel boiler designs (1990-2000)” has been a result of a long development process. Mathematical furnace models based on computational fluid dynamics (CFD) have been developed since the early 1980s and a great number of research groups at universities and companies have contributed to the advancement of these modelling techniques. The main development – including creation of several commercial CFD codes – was initially focused on furnaces fired with gas, oil or pulverized coal. However, black liquor recovery boilers have required a lot of additional creative development due to the many specific processes that differ significantly from the conventional combustion systems.

This work, specific to recovery boilers, was started already in the late 1980s. The two first publications on recovery boiler furnace modelling were presented at the International Chemical Recovery Conference (ICRC) in 1989. One originated in research from the Institute of Paper Chemistry (today IPST), and the other was a joint paper by Tampere University of Technology together with the boiler manufacturer Tampella at that time (today Valmet) (Grace et al. 1989, Upptsu et al. 1989). Tom Grace concluded his paper by some words concerning the computing times: “Convergence is a major problem. - About three months of CPU time were needed for the base case on a MicroVAX II.” A few years later, in 1996, Tom Grace wrote the first review on computer modelling of black liquor recovery furnaces (Grace 1996).

Later, many other groups have contributed to this development including the University of Toronto, Helsinki University of Technology (today Aalto University), VTT and Åbo Akademi University in Finland, the Royal Institute of Technology in Sweden and several company groups. By now, some 200 papers concerning numerical modelling of the recovery furnace have been published. Today, the worst bottleneck is no longer the computing time. The biggest challenges are connected to the detailed descriptions of the many physico-chemical processes taking place in the furnace, the so-called submodels to be included in the general flow model. Such recovery boiler-specific processes that have required special development include:

- Liquor spraying (course droplets)
- Liquor droplet burning behaviour (very different from any other fuels)
- Fate of the molten inorganic chemicals remaining after burn-out
- Formation/consumption of the char bed
- Gaseous chemistry of nitrogen and sulphur

Detailed calculation models to predict the gas flows and combustion in recovery furnaces have been a very important contributor to the development of the recovery technology. The models are today used as a standard tool when new boiler design features are considered, or when operational problems in existing boilers are addressed. The courageous dramatic scale-up of the boiler sizes that has taken place during the very recent years would not have been possible without thorough model studies using advanced CFD models.

Panel comments:

“CFD has been of great help to the boiler manufacturers...has helped to optimize air system and boiler dimensions”

“A tool to allow planning of bigger and bigger boilers”

Some challenges were also pointed out:

“Char bed still a black hole in CFD…”

“A drawback in CFD is that different tools give different results (WYWIWYG = what you want is what you get)”

Effort 5. High solids firing

Liquor solids content strongly influences the overall boiler efficiency. Consequently, the vaporization plant technology has been in the focus of continuous improvement work since the early days of the Kraft recovery technology. However, in the 1980s this development jumped to a new level when the technology allowed liquor solids contents to exceed 70%, and later even 80%.

This “Research on development of high solids firing – for better furnace behaviour and lower SO2 emissions (1980s)” was initially strongly driven by the boiler or evaporator manufacturing companies (Hyöty & Ojala 1987, Ryham 1989). Later many research organizations such as KCL, Åbo Akademi University and VTT in Finland were involved in studying the many details and effects of the high solids firing.

It was soon recognized that, besides the energy efficiency benefits, this “high solids firing” changed the recovery boiler process much more than expected. In fact, the changes in the furnace and flue gas operation were quite dramatic. Liquor firing and bed control became significantly easier. However, the most remarkable effect of the high solids firing was the practically complete elimination of the SO2 emission in boilers when liquor solids content exceeded some 73-75%. This effect was shown to be connected to the higher temperatures in the lower furnace caused by the smaller amount of water entering the furnace along with the liquor. The higher furnace temperature resulted in a dramatically better capture of sulphur dioxide by sodium vapours released during combustion.

The elimination of SO2 from the flue gases caused further changes in the furnace and flue gas chemistry. The dust particles became alkaline and sticky dust problems, caused by formation of acidic sulphates, disappeared. Also
the fate of chlorine changed, in high solids firing all chloride stays in the solid dust and any purge of chlorine in the form of HCl in flue gases stopped. Interestingly, it was later shown that the high solids firing could well be realized without any significant increase in the NOx emissions.

The panel comments were unanimous:

“High dry solids firing has been one of the major development steps in RB history”

“It solved the SO2 emissions, increased the efficiency of the boiler, etc.”

“The dramatic reduction in SO2 emissions also forced us to try to understand the NO-S chemistry during combustion. Nobody understood why SO2 disappeared from flue gases with high dry solids firing.”

Interestingly, one panel member questioned if, or to what extent, this development was a result of targeted research efforts:

“Significant thing for the control of sulphur emissions. However, it probably had advanced gradually along with practical experiences as well.”

The next five highest-ranking research efforts

Effort 6. NOx formation

Formation mechanisms of nitrogen oxide emissions in black liquor combustion were shown to differ from combustion of other fuels in many respects. The “Research on the fate of BL nitrogen in combustion and theoretical basis for furnace NOx reduction strategies (2000)” started already in mid 1990s but became very active in the 2000s.

Even if the nitrogen content in the liquors is quite low, typically around 0.1%, it appeared that the absolute majority of the nitrogen oxides, NOx, formed in a recovery furnace originated from that. The reaction pathways of this black liquor nitrogen in the combustion became a highly interesting and demanding research topic. The single droplet burning tests at Åbo Akademi University shed light on the issue (Aho et al. 1994). It was shown that, during the devolatilization, a part of the black liquor nitrogen, typically 20-30%, was released as ammonia. This ammonia very readily formed NO when the volatile gases were oxidized in the upper furnace.

The truly surprising finding was that some part, typically 20-40% of the black liquor nitrogen could end up dissolved in the smelt. This nitrogen was identified as sodium cyanate, NaOCN. Some of the first mill measurements showed that the distribution of the nitrogen into NO or smelt cyanate can be strongly influenced by boiler operation (Savijärvi & Aho 2006).

In the dissolving tank and the green and white liquors this cyanate gradually converts to ammonia. This ammonia was shown to be a potential source of uncontrolled emissions — depending on the details of the recovery process of the mill.

Interestingly, the European panel members graded this research clearly higher than the North American members.

“NOx chemistry is an important topic, since stringent emission limits are also applied to recovery boilers and combustion control is still the only BAT (Best Available Technology)”

“Complicated chemistry and kinetics play a major role in NOx formation.”

“Important research. Based on this the NOx emissions could be predicted better than before. The results were directly applicable in practice.”

The panel members also mentioned the unresolved challenge of the quantitative prediction of NO emissions:

“Some NOx chemistry has been incorporated into CFD models, but still an unresolved area in black liquor combustion chemistry…”

“….models are not able to predict N behavior in the furnace”

Effort 7. Alkali chloride induced corrosion

The maximum steam temperatures in recovery boilers are just above 500 °C. This is significantly lower than in boilers burning conventional fuels; in these boilers the steam temperatures can be above 600 °C. The lower steam temperature results in lower power production efficiency. Consequently, there is a great interest in the possibilities of increasing the steam temperatures in recovery boilers. The higher steam temperatures have been limited by high-temperature corrosion induced by the fireside deposits containing alkali chlorides.

“Research on alkali chloride induced superheater corrosion mechanisms to pave the road for higher steam temperatures (2000-2010)” has been a topic for research for long and many research groups have contributed with various studies.

Oak Ridge National Laboratory, Paprican (today FPInnovations), VTT, University of Toronto and Åbo Akademi University have been the most active ones. Many research techniques have been applied. Laboratory exposure furnaces have been used to systematically study the influence of various factors on the salt-induced corrosion. Air-cooled probes have been used to test materials in the superheater section of boilers.

Recent work has come up with a number of interesting new findings. Even extremely small amounts of chloride in the alkali salt deposit has been shown to dramatically initiate corrosion on a variety of steel qualities (Skrivvars et al. 2008). The deposit first melting temperature has been shown to give the upper limit to the material temperature in the superheater, which has given one useful guideline for the design of the material temperatures in the superheater. However, the presence of chlorides may cause corrosion also at material temperatures below the first melting point, and at these conditions the corrosion criteria are less well under control. Relevant new research results concerning the corrosion effects of alkali chlorides have also been obtained by groups working with superheater corrosion in boilers fired with solid biofuels. In these boilers the key compound causing corrosion is potassium chloride. The corrosion mechanisms of the two alkali chlorides appear to be quite similar (Enestam et al. 2013). The very first step in the corrosion of stainless steels by alkali chlorides appears to be formation of alkali chromates, which causes the break-up of the protective chromium oxide layer (Petterson et al. 2005).

The understanding of the corrosion mechanisms has increased significantly. With this knowledge the reasons for corrosion patterns in boilers can in most cases be explained. However, the research has not yet produced any direct solutions to allow clearly higher steam temperatures in an alkali chloride environment.

Also in this research the European evaluation was more positive than the North American:

“Important to the control of superheater corrosion and increase of the power production. Results can be immediately applied.”

“This together with the ability to predict fly ash behaviour is essential in increasing the power output from recovery boilers.”

Some questions were also raised:

“Why is 515 °C still the upper limit for steam?”

“Why do austenitic steels behave well in superheaters, but low-alloyed steels do not?”

Effort 8. Acid sulphates

The formation of acid sulphates may make the flue gas dust sticky and corrosive in the cooler part of the flue gas channel. Acid sulphate formation is a well recognized problem in boilers with a high SOx content in the flue gases. The research here entitled “Exploring the factors governing the formation of acid sulphate in the dust for control of sticky ash (1980-90)” was initiated already in the late 1970s in Sweden by the
Swedish Pulp and Paper Research Institute STFI (today Inventa) and AF, and in Finland by the boiler manufacturer Tampella (today Valmet). The initial work was connected to boilers burning sodium sulphite liquor. In these sodium sulphite recovery boilers the SO₃ content in the flue gases is very high and the acid sulphate formation was recognized first. Later, the acid sulphates were found in kraft boilers as well. Åbo Akademi University and the University of Toronto continued the initial work, which gradually revealed the mechanisms of acid sulphate formation and factors affecting the formation (Backman et al. 1984, Poon et al. 1993).

The sticky ash is formed when low melting sodium bisulphate NaHSO₄ is formed on the surface of the dust particles. The bisulphate is formed via a reaction with sulphur trioxide SO₃ (2000–2010) researchers from the IPST and the University of Helsinki showed that the sulphite boilers only:

Different experimental techniques have been developed to characterize real black liquor sprays by advanced video recording etc. Tests have been performed in special spray chambers but recently also in furnaces (Miikkulainen et al. 2008). Significant new information has been produced on factors affecting spray behaviour and droplet formation mechanisms. Droplet size and velocity distributions have been mapped under a variety of conditions (Figure 6). Attempts are also made to further understand the liquor behaviour in the nozzles by advanced flow modelling (Levesque et al. 2004).

The panelists gave somewhat mixed comments:

“Black liquor spraying has been studied since the 1990s and it is an important topic still.”

“One of the key issues for successful combustion of black liquor, especially in large furnaces.”

“Liquor droplet formation has been extensively studied, with good results but just small impact to the practice.”

**Effort 10. Partial autocaustization**

Many ideas have been suggested to change the recovery boiler process in such a way that the causticizing step could be partly or completely eliminated. This can be achieved with a suitable added substance, which changes the smelt composition in such a way that no or less carbonate is formed (Jansson 1997).

In the 2000s there was a great interest in the use of boron compounds to produce such an autocaustizing effect. The research in “Partial autocaustization using boron (2000)” was initiated by the U.S. Borax Company and the first key publications came from the University of Toronto. Later, among others Åbo Akademi University, the Oregon State University and the University of Luleå made a number of studies around boron autocaustization.

The boron-based autocaustization implies adding in the black liquor sodium metaborate, NaBO₂, which reacts with the smelt sodium carbonate forming a more sodium rich borate. When dissolved in the dissolving tank this borate directly forms sodium hydroxide and converts back to the metaborate. The metaborate is fully soluble and will follow the recovery solutions all the way to the digester and further to the black liquor and back to the boiler. This way the borate is recycled and used again, and new borate is only needed to cover any chemical losses from the cycle (Figure 7).

The research included laboratory experiments and thermodynamic modelling of the exact stoichiometry and yield of the smelt-borate reactions at different conditions (Lindberg & Backman 2004). It also included studies on the potential changes in the boiler dust composition and properties caused by the boron addition (Hupa et al. 2002). Finally, the partial autocaustization was tested and applied in full scale in several boilers (Ellis & Kochesfahani, 2005).

In spite of the creative research efforts made, the boron technology has found only limited use in practice. The panel also noted this:

“This is a topic that only a limited number of mills were interested in.”

“... did not actually solve the bottleneck problems at the mills.”

“It lived for a while, but the interest died quite rapidly.”

“Limited application.”

**Concluding Remarks**

The development of the recovery boiler technology has been impressive. Modern boilers are remarkably clean, reliable and – huge in size. Important contributors to this development are the many long-term research efforts by a number of people all over the world. This paper wanted to salute this successful research by reviewing ten examples of efforts that have significantly helped to improve the design and operation of the recovery furnace process. A common feature with the examples qualifying to this “top-10” list was that for all of them it took many years – typically a decade - of active work before they finally produced results which could be used in the industry.
Besides the ten examples described above, several other suggestions received support from the evaluation panel:

- Research on char bed cool-down mechanisms and means to accelerate cool-down.
- Removal mechanisms of soot blowing, and the development of high-efficiency soot blowers.
- Research showing the role of the smelt freezing temperature on smelt viscosity and the formation of the so-called jelly-roll smelt.
- Research on sodium and sulphur release and dust formation, the historical interrupted combustion tests at Rauma and Kaskinen showing that most of the fume is formed during in-flight and only a minor part is coming from the char bed.
- Composite tube cracking – a major problem which now has been cured by the use of correct materials.

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References


Figure 7. Partial autocastization using boron additions (Tran et al. 1998).
Recovery boilers are built all over the world. The roots of recovery technology are longer than the roots of recovery boilers. But it wasn’t until the invention of recovery boilers before the Second World War that the pulping technology was revolutionized. This led to long development of essentially the same type of equipment, culminating into units that are largest biofuel boilers in the world.

Early recovery technology concentrated on chemical recovery as chemicals cost money and if one could recycle these chemicals then the profitability of pulp manufacture would improve. For pulp mills the significance of electricity generation from the recovery boiler was for long secondary. The most important design criterion for the recovery boiler was a high availability. The electricity generation in recovery boiler process can be increased by elevated main steam pressure and temperature or by higher black liquor dry solids as well as improving its steam cycle. This has been done in the modern Scandinavian units.

Early recovery technology

Early recovery technology concentrated on chemical recovery (Deeley & Kirkby 1967). Chemicals cost money and it was easy to discover that recycling these chemicals would improve the profitability of pulp manufacture (Vakkilainen 2005). Recovery of pulping chemicals could be based to French chemist Nicholas LeBlanc’s process for producing soda at reducing furnace. A flame oven was hand filled with black liquor, Figure 1. After that, the black liquor was dried with flue gases from burning wood. The dried black liquor was then scraped to floor, collected and sent to separate smelt pot, Figure 2, for reduction and burning the remaining organics (Rydholm 1965). Recovery of chemicals with this type of system was inefficient. Chemicals recovery hardly exceeded 60% (Whitney 1968).

Figure 1. Early flame oven from late 1800s (Edling 1981).

Figure 2. Early smelt pot from late 1800s (Edling 1981).
Hand operated recovery grew more complicated with additional heat recovery surfaces. Pre-evaporation and scrubbing in a rotary device was invented by Adolph W. Waern (Combustion Engineering 1949). The direct contact evaporator improved the heat economy of the recovery system. The hand feeding operation was soon replaced by rotary oven, Figure 3.

![Figure 3. Rotating oven from 1890, liquor in at 20% ds (Edling 1981).](image)

Use of rotary oven improved the heat economy. Then it was a small step to introduce heat recovery equipment as was done with other types of boilers at that time. In 1912 the S-S system (Sundblad-Sandberg) was taken online at Skutskär. In this system, liquor was sprayed into rotary furnace at 50% ds. The evaporation and scrubbing in a rotary device was recovered with vertical tube boiler.

The boilers parts were improved on. In 1930 seven LaMont type forced circulation units were built. The use of rotary furnaces pinnacled in Murray-Waern type units which were successfully built around the world. In these the rotary precombustion was combined with totally water-cooled furnace with lower part refractory lined. The Murray-Waern recovery units were popular until the fifties.

Tampella was among the first manufacturers to build S-S type furnaces, Figure 4. Preventing unnecessary air flow through sealing arrangement between rotary drum and fixed parts was one of the major operating problems. The combustion was often conducted at very high air ratio leading to inefficient energy use. One could generate 3000-4000 kg of 3.0 MPa steam for each ton of pulp (Roschier 1952).

The main recovery equipment itself remained unchanged, but details were improved on. Smelt dissolving tank was introduced, final smelting was improved on and capacities grew. The use of refractory and rotary oven tended to limit the recovery capacity to 70-75 tds/d (Sebbas et al. 1983). Rotary part lengths were 7-10 m and diameter about 1.5 m (Swartz & MacDonald 1962).

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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 changing spray proved easy. Stationary spraying was used in early rotary furnaces and with some success adapted to stationary furnace by H. K. Moore (Toivanen 2012). Thirdly one can control the charbed by having primary air level at charbed surface and more levels above. Multiple level air system was introduced by C. L. Wagner.

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.

After several attempts and learning from co-operation with Wagner when they built a stationary recovery furnace at the soda pulp mill of Howard Smith Paper Mills Ltd., in Cornwall, Ontario, Tomlinson built and put into service his first experimental stationary furnace with a heat recovery boiler in 1929 (Steam 1992). This was soon followed by the world’s first recovery boiler unit with completely water cooled furnace at Windsor Mills which started operation on June 27, 1934 (Tomlinson 1975). After reverberatory and rotating furnaces the recovery boiler was on its way (Jones 2004). Recovery boiler had two substantial benefits. One could build more easily larger recovery boilers than rotating furnaces. The second was energy efficiency.

In Finland Oulu Mills invested in the first five 120 tds/d recovery boilers in 1937. They followed in the footsteps of Husum 1936 and Skutskär 1937 which both had invested in similar recovery boilers. Kotka mills meanwhile invested in rotating furnaces. When the energy efficiency of recovery boiler and rotating furnace was investigated it was found that recovery boiler could produce 5000-5300 kg/ADt steam when rotating furnace could produce only 4500 kg/ADt. The most modern boilers produce 4500 kg/ADt (Fernandez 2001; António 2011). The early recovery boilers had net efficiency of about 70% (LHV).

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. The first CE recovery unit, looks a lot like a modern recovery boiler.

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*1.1 m at superheater entrance (Pettersson 1983). 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. One of the early Scandinavian boilers 160 t/day at Korsnäs, operated still almost 50 years later (Sanquist 1987). Edling states in 1937 that more than 20 units had already been built of which 10 in Scandinavia.

Development of recovery boiler technology

Spread of Kraft recovery boilers was fast as functioning chemical recovery gave Kraft pulping an economic edge over sulfite pulping (Boniface 1985). They had about 20% better energy efficiency as more than 5000 kg of 3.0 MPa steam for each ton of pulp could be generated (Roschier 1952, Alava 1955). The first recovery boilers had horizontal evaporator surface followed with superheaters and more evaporation, Figure 5-6. These boilers resembled the state-of-the-art boilers of some 30 years earlier. This trend has continued until today. It is easy to understand that when any stop will cost a
The first recovery boilers had severe problems with fouling (Deele & Kirkby 1967, Roschier 1952). Tube spacing wide enough for normal operation of a coal fired boiler had to be wider for recovery boilers. This gave satisfactory performance of about a week before a water wash. Mechanical steam operated sootblowers were also quickly adopted. To control chemical losses and lower the cost of purchased chemicals electrostatic precipitators were added. Lowering dust losses in flue gases has more than 60 years of practice. One should also note the use of electrostatic precipitators in an early Finnish recovery boiler, Figure 6 (Roschier 1952). The air levels in recovery boilers soon standardized to two. The primary air level was placed at the char bed level and the secondary above the liquor guns.

In the first tens of years the furnace lining was often of refractory brick or refractory on cast blocks. The flow of smelt on the walls causes extensive replacement and soon designs that eliminated the use of refractory were developed. The standard then became the tangent furnace wall. Membrane wall use became widespread in the 1960s.

B&W favored use typically a single black liquor gun at front wall. In larger units additional gun was placed on back wall (Tomlinson & Richter 1969). They preferred a significant part of the liquor to be sprayed to walls for drying. Boiler bottom was in angle causing smelt to flow quickly out. Hardly any space was reserved for smelt layer in the furnace. Thus this kind of furnace is named sloping bottom type. Final black liquor evaporation was often carried in a direct contact evaporator of venturi scrubber or cyclone evaporator type. The highest practical black liquor solids was 60-65% depending on black liquor properties. Use of wall spraying was promoted by B&W and its licensees Götabverken and Babcock Hitachi. B&W adopted three level air in the late 1960s.

Early on the CE design stressed use of multiple guns in all walls (Tomlinson & Richter 1969). Boiler bottom was flat with space for smelt layer on top of the whole floor. Thus this kind of furnace is named decanting floor type. Final black liquor evaporation was carried in a direct contact evaporator of cascade evaporator type. The basic aims of recovery boiler design could soon be summarized as; highest possible recovery of chemicals, high efficiency, high utilization of the calorific values in black liquor and highest safety of operation (Hochmuth, 1953). CE stucked for a long time with a two level air system that had corner fired secondary. They used similar system in PCF-boilers.

There are some early examples of single drum recovery boilers. Both B&W and Ahlstrom delivered a single drum boiler in the late 1950s. The first modern single drum recovery boiler was delivered in 1984 by Götabverken to Leaf River at Hattiesburg, Mississippi. The boiler size was 1966 tds/d. By 1990 all manufacturers started providing single drum boilers. Excluding very small boilers, all modern boilers are now of single drum design.

There are several advantages in a single drum boiler. Single drum construction eliminates the possibility of water leakage to furnace as it is placed outside the furnace. There are significantly less holes in a drum wall. Therefore it can be built thinner. Thinner wall of drum allows faster startup and stop-down. The gas flow to the boiler bank is smoother and heating surface arrangement is simple. The erection period is shorter because of large block construction. There is no rolled tube work. Enhanced and steady water circulation by separated and unheated downcomers. The largest advantage is that single drum boilers can be made larger. Tube stiffness limits cross flow two drum arrangement to about 2300 tds/d size (Steam 1992). Vertical flow twodrum constructions have suffered from plugging because of vibration stiffeners.

First recovery units had brick lined lower furnace with straight tubes forming cooling section behind bricks. This design persisted until the 1960s. Some of these units are still operating today. Another design provided corrosion protection of furnace tubes with studs and refractory. Some manufacturers use studs even today, but the need of stud replacement has led to decline in stud use. From late fifties onwards the membrane wall design took over, first with carbon steel walls. Tangent tube design was replaced with membrane design. The drawbacks of tangent design were the difficulties in inspecting welds and doing maintenance work.

First furnace walls were of carbon steel. With increasing design pressure there were several corrosion problems in lower furnace. The advantage of chrome containing alloys as wall corrosion inhibitor was discovered as an answer to high pressure boiler sulfidation corrosion (Moberg 1974). In 1972 Tampella delivered first totally compound tube recovery boiler furnace to ASSI Lövholmen mill in Piteå, Sweden. By 1982 there were 30 recovery boilers with AISI 304 compound tube bottoms in Scandinavia (Westerberg 1983). Use of composite tubing in United States started as late as in 1981.

Sanicro 38 is a widespread material that offers improved corrosion protection for lower furnace. The first lower furnace made from Sanicro38 was delivered by Valmet. They used Sanicro38 in the lower furnace up to primary ports in 1994 for their Rauma recovery boiler.

Figure 5. First Tomlinson kraft recovery boiler with water cooled furnace from Babcock & Wilcox in 1934. Note spray tower using weak black liquor before the ID fan.

Figure 6. Early Finnish recovery boiler (Roschier 1952).
of vertical flow design the gas flows downwards and water counter currently upwards (Hyöty 1994). In a period of few years the current long flow economizer design emerged, Figure 7 (Moberg 1967). Vertical economizer design spread fast in Scandinavia where by mid 1970’s more than a half of the recovery boilers had long flow economizers without direct contact evaporator (Environmental 1976).

In competition to purely vertical, the three pass design featured gas flow which was forced crosswise the economizer tubes to improve heat transfer.

There have been several rounds of economizer header designs. In a typical old design each economizer tube is connected to a common large header. As maximum number of tube rows that fit to this type header is about 8-10. The larger economizers must have front and back headers. This design has the disadvantage of having a header in the gas flow. The header can corrode and the welded joints tend to receive thermal stress. Modern economizers have flat horizontal headers.

**High dry solids**

Dry solids at as fired black liquor was between 60 and 65% in Sweden in the beginning of the 1960s (Jönsson 1961). In the beginning of 1950s the typical as fired black liquor concentration was 50% (Vegeby 1961). The final concentration was often done with cascade or cyclone evaporator. In practice the as fired dry solids could remain dangerously low before refractometers started to be applied in late 1960s and early 1970s (Hellström 1970). The only reasons seen for higher dry solids were the energy economy and increase of bottom loading (Vegeby 1961). One advantage noted was that partial load capability improved with higher dry solids. Increasing black liquor dry solids from 60% to 68% enabled running recovery boiler without auxiliary fuel firing at 65% of rated MCR (Rissanen 1965). At 60% dry solids hardly any partial load could be run.

In 1980s the first high dry solids’ units started their coming on line. Extensive tests of effect of increasing dry solids from 72% to 84% were run at Metsä-Botnia Kemi and Rosenlew, Pori (Finland) recovery boilers (Hyöty & Ojala 1987). They noticed that above 75% dry solids the SO2 and H2S emissions were practically zero. Also reduction increased more than one percentage point. Other benefits listed were, that steam generation and boiler controllability increased. High dry solids require that ESP ash is mixed to the black liquor with 62-65% liquor. Higher retention time also improves the stability of resulting black liquor.

**Improving air systems**

Air system development continues and has been continuing as long as recovery boilers existed (Vakkilaainen 1996). As soon as the target set for the air system has been met other new targets are given. Currently the new air systems have achieved low NOx, but are still working on with lowering the fouling.

The first generation air system in the 1940s and 1950s consisted of a two level arrangement; primary air for maintaining reduction zone and secondary air below the liquor guns for final oxidation (Linares & Chapman 1989). The recovery boiler size was 100-300 tds/d and black liquor concentration 45-55%. Frequently to sustain combustion auxiliary fuel needed to be fired. Primary air was 60-70% of total air with secondary the rest. In all levels openings were small and design velocities were 40-45 m/s. Both air levels were operated at 150 °C. Liquor gun or guns were oscillating. Main problems were high carryover, plugging and low reduction. But the main target, burning of black liquor could be done.

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<thead>
<tr>
<th>Air system</th>
<th>Main target</th>
<th>Additional targets</th>
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<tr>
<td>1st generation</td>
<td>Stable burning of black liquor</td>
<td></td>
</tr>
<tr>
<td>2nd generation</td>
<td>High reduction</td>
<td>Burn liquor</td>
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<tr>
<td>3rd generation</td>
<td>Decrease sulfur emissions</td>
<td>Burn black liquor, high reduction</td>
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<tr>
<td>4th generation</td>
<td>Low NOx</td>
<td>Burn black liquor, high reduction and low sulfur emission</td>
</tr>
<tr>
<td>5th generation</td>
<td>Decrease superheater and boiler bank fouling</td>
<td>Burn black liquor, high reduction, low emissions</td>
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The second generation air system targeted high reduction. In 1954 CE moved their secondary air from about 1 m below the liquor guns to about 2 m above them (Linares & Chapman 1989). The air ratios and temperatures remained the same, but to increase mixing 50 m/s secondary air velocities were used. CE changed their frontwall/ backwall secondary to tangential firing at that time. In tangential air system the air nozzles are in the furnace corners. The preferred method is to create a swirl of almost the total furnace width. In large units the swirl caused left and right imbalance. This kind of air system with increased dry solids managed to increase lower furnace temperatures and achieve reasonable reduction. B&W had already adopted the three level air by then.

At first the airport openings were made by bending one tube away from the opening sideways and making room for this by bending another tube back. Airport width was about tube spacing and large plate areas were needed to make aircraft gas tight. In 1978 CE began experiments with two level primary air. Upper primary was designed to about 20% of total air with velocity up to 60 m/s. Total air split remained the same. The aim was to increase hearth temperatures.

Third generation air system was the three level air. In Finland the use of three level air with primary and secondary below the liquor guns started about 1980. At the same time stationary firing gained ground. Use of about 50% secondary seemed to give hot and stable lower furnace (Westerberg 1983). Higher black liquor solids 65-70% started to be in use. Hotter lower furnace and improved reduction were reported. With three level air feed and higher dry solids the sulfur emissions could be kept in place.

Earlier the recovery boilers had horizontal tube economizers. They plugged fast and had to be water washed at intervals of 1-4 weeks (Rissanen 1965). It was not until the early 1960 that installing vertical economizers started. In economizers
Fourth generation air systems are the multilevel air and the vertical air. As black liquor dry solids to the recovery boiler have increased, achieving low sulfur emissions is not anymore the target of the air system. Instead low NOx and low carryover are the new targets.

The three level air system was a significant improvement, but better results were required. Use of CFD models offered a new insight of air system workings. The first to develop air system with additional air levels was Valmet (Tampella) in 1990 multilevel secondary air in Kemi, Finland, which was later adapted to a string of large recovery boilers (Mannola & Burel 1995). Valmet also patented the four level air system, where additional air level is added above the tertiary air level. This enables significant NOx reduction.

Meanwhile Andritz adopted vertical air where primary level is arranged conventionally. Rest of the air ports are placed on interlacing 2/3 or 3/4 arrangement. Vertical air was invented by Erik Uppstu (1995). His idea is to turn traditional vertical mixing to horizontal mixing. Closely spaced jets will form a flat plane. In traditional boilers this plane has been formed by secondary air. By placing the planes to 2/3 or 3/4 arrangement improved mixing results. Vertical air has a potential to reduce NOx as staging air helps in decreasing emissions (Forssén et al. 2000).

**High temperature and pressure recovery boiler**

Development of recovery boiler main steam pressure and temperature was rapid in the beginning, Figures 8-9. By 1955, not even 20 years from birth of recovery boiler highest steam pressures were 10.0 MPa and 480 °C (Vakkilainen et al. 2004). The typical pressures and temperatures then backed downward somewhat due to safety (McCarthy 1968). By 1980 there were about 700 recovery boilers in the world (Westerbeg 1983). In Japan, because of high electricity prices, more than ten high temperature and pressure recovery boilers are in use (Tsuchiya et al. 2002). The biggest one is the 2700 tds/d, 10.3 MPa and 505 °C recovery boiler at Iwakuni mill (Ohtomo 2000).

New large recovery boilers seem to favor high main steam temperatures and pressures (Vakkilainen 2004). These increase the amount of backpressure electricity.

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**Main steam temperature**

Maximizing electricity generation is driving increases in the main steam pressures and temperatures. The maximum steam temperature can be limited by the ash properties. The first melting curve at the superheater front should be taken into account. Increasing mill closure with high chlorine and potassium decreases the melting temperatures. The overall mill heat balance should be used to optimize the feed water and flue gas temperatures.

The main steam temperature of recent recovery boilers is shown in Figure 9 as a function of MCR capacity of that boiler. The average steam temperature increases with size. Small boilers tend to have lower pressures to reduce specific cost. There are many boilers with main steam parameters higher than 500 °C. Most of them are in Japan.

**Future high energy efficiency recovery boiler**

The increase of power generation in a pulp mill is result of larger recovery boilers being built (Haaga 2014). The widely adopted industry practice of rising the black liquor dry solid content and main steam parameters will change the recovery boiler to sellable energy generator (Heinola 2014). The rise of main steam parameters after superheaters from 90 bar/490 °C to 100 bar/505 °C increases generated power 2%. When increasing steam parameters and increasing black liquor dry solid content from 75% to 82% the generated power increases by more than 6%.

Often neglected way to increase generated power is the low-pressure preheating of turbine condensate and demineralized water to 100 °C by turbine condensing section bleeds. This increased generated power by some 3% due to reduction of low-pressure steam extraction for water heating in feed water tank.

The rise of feed water temperature from 115 °C to 140 °C was the next attempt to increase power generation. It requires only small investments. It did not increase the generated power due to the higher flue gas losses. The high-pressure preheating of feed water to 180 °C has even worse effect on generated power due to the heat losses of the flue gases. The solution is to increase the economizer surface areas or to add a heat. The flue gas heat recovery devices have high investment costs, but they are still highly recommendable. Using flue gas heat recovery devices with other alternatives can increase their effect significantly. The combination of combustion air / demineralized water heating and feed water
preheating has the best result increase of generated power. The gain is because use of extraction steam can be reduced. These combinations have short payback periods in slightly more than one year.

The coupling using high-pressure preheating and combustion air heating means significantly increased generated power. This combination reduces high-pressure steam extraction significantly. Adding high-pressure preheating increases investment about 1 M€ and has a negative payback period.

The combustion air heating to 190 °C increases generated power due to higher steam flow. The investment cost of an additional steam/air unit and modernization of power generation equipment is 1 M€. Payback period is in our case a few months. The energy improvement’s efficiency can be increased through combinations with alternatives of feed water heating and flue gas heat recovery. These combinations reduce payback period to 11-13 months due to increase of generated power.

The combination of all energy improvements can increase generated power more than 15%. This requires an additional investment of more than 11 M€ but gives payback period of approximatively one year depending on flue gas recovery application used.

Hence, the total optimization of pulp mill can increase generated power up to 23 MW with a payback period of the additional investment being 13 months. When calculating at a net sale price rate of 50 €/MWh it will create an additional profit of 10 M€/year from additional saleable products such as biochar.

Conclusions
The energy efficiency of recovery boiler process can be improved by:

- New modes of operation such as improvement of skills and motivation of personnel, energy audits, enhanced process integration of existing processes and industrial plants (secondary heat), collecting of reliable process information (monitoring and control) and decreasing sootblowing steam usage.
- New technology such as higher steam pressure and temperature, higher firing liquor dry solids and adopting electricity increasing features known from general boiler technology (increased feed water temperature, increased air preheating, flue gas heat recovery).
- New processes such as additional firing (e.g. bark or chips) and combining torrefaction or bio-oil production with recovery boiler.

Figure 10 shows recovery boiler integrated with torrefaction (Hamaguchi et al. 2013b). If we can adopt our recovery operation to produce additional saleable products such as biochar, then changes are to be expected.

The recovery boiler operation will be affected by changes in pulping process such as lignin removal and hemicellulose removal, Figure 11 (Hamaguchi et al. 2013a).

Modern Kraft recovery boiler has evolved from chemical recycler to energy generator to providing sellable power. With next ten years even more radical changes are expected.

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Introduction

In 1936 a design of spray furnace was suggested in which the boiler was mounted above the smelter furnace in a tower arrangement. The design gave many advantages and reduced the need for manual labor (de Lorenzi 1949). Rotating furnaces were replaced by spray furnaces in future designs. Spraying enabled control of the char bed and combustion by changing the spray direction and pressure. The mass flow rate and droplet size could be easily changed. The air distribution to the char bed could be connected to the spraying (Vakkilainen 2007).

In Finland, the first Tomlinson type boilers were built in the 1930s and 1940s (Vakkilainen, 2007). Obviously, a few of them were using oscillating nozzles to spray evenly in all parts of the furnace. It was normal to spray on furnace walls to a dry black liquor for better combustion. In the 1980s, stationary firing became the dominant way of spraying black liquor, first in Europe and later in the U.S. (Llinares & Chapman 1989). Splash plate nozzles were common, but swirl cone nozzles were used in small boilers.

The transition to higher solids content black liquors started during the 1980s. It had many advantages. The most important is the increased throughput capacity of a recovery boiler, which is often the bottleneck in a pulp mill. Other advantages are better sulfur reduction, higher energy production, decreased emissions, and decreased risk of smelt explosion. The nature of spraying changed with increased solids content. Higher black liquor temperature was needed to decrease viscosity, and sometimes spraying temperature was above the boiling point of black liquor. The spraying temperature was often above the boiling point, although boiler operators were not aware of flashing. Liquor heat treatment processes were also developed to decrease viscosity and avoid firing temperatures that were too high.

The importance of spraying studies was emphasized by the volume of heat and power generation from black liquor burning. In Finland, almost 11% of primary energy was supplied by black liquor combustion in 2001. This was important in the viewpoint of the Kyoto agreement under which CO₂ emissions were restricted. The combustion of forest-based black liquor could be calculated to be neutral concerning CO₂ emissions. Tightening emission regulations caused an increased need for better combustion control.

Boiler sizes have been increasing year by year, and therefore the cost of shutdowns and other problems have also been increasing. The value of produced steam and electricity has been increasing all the time. The need to better understand the recovery process increased; and at the same time, new research findings in other research fields became available. The same development was seen in black liquor spraying studies starting in the late 1980s. Active research on black liquor spray started in the U.S., Canada and Finland.
Experimental studies

Many studies have been carried out to simulate the spraying of fuels and other liquids. Most often, the purpose of spraying is to atomize a single component liquid to very small droplets with a large surface area and high reactivity. The prediction of spray properties is at a good level for these liquids and nozzles. In the case of black liquor, the liquid is very challenging. The solids content is high, and a very high number of different organic and inorganic species is included. The goal of spraying is to produce a proper droplet size for drying and devolatilization, distribute the char and solids evenly to the char bed, and produce good combustion. The properties of black liquor and the goals of spraying have led to different nozzles that are uncommon in other fields of spraying. Experimental studies and detailed modeling have been necessary to increase the understanding of black liquor spray properties.

After 1985 a large set of experimental studies have been carried out. Figures 1 and 2 show most of the experimental studies carried out with substitute fluids and with black liquor. The relevant operational range in modern furnaces is located between the green dashed lines. Smaller nozzles, lower spraying temperature, and lower solids content experiments carried out in Canada and the U.S. are often relevant to older furnaces.

Most of the published experimental studies are carried out at the Institute of Paper Technology and Science (IPST) or at Aalto, formerly the Helsinki University of Technology. The industrial scale tests have been carried out mostly at Aalto. Small commercial nozzles have been studied at IPST. The University of British Columbia (UBC) and Tampere University of Technology (TUT) were among the first during the last two decades to study black liquor spraying. Substitute fluid tests with splash plate nozzles have been carried out by the University of Toronto (UoT) during the latest decade.

Table 1 lists the nozzles, mass flow rates, and fluids studied. Some of these studies concentrate on the sheet breakup, some concentrated on the measurement of droplet size, and some concentrated on the spray velocity. An overall view of the research in this field can be found in Figures 1 and 2, where fluid properties, nozzle sizes, and mass flow rates of different research projects are presented. Experiments with substitute fluids are presented in the lowest part of the chart in Figure 2.

<table>
<thead>
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<th>Table 1. Black liquor spraying studies.</th>
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<tr>
<td>Bennington and Kerlos, UBC</td>
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<td>Mäntyniemi, TUT</td>
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<td>Adams et al., IPST</td>
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<td>Paloposki and Kankkunen, Aalto</td>
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<td>Mikola et al., Aalto</td>
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<td>Karouzi et al., UoT</td>
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* D = drop size, v = velocity, bm = breakup mechanism
** W = water, WG = water/glycerol mixture, S = syrup, BL = black liquor

Droplet size, shape, and size distribution

The size and shape of a black liquor particle depends on its drying, combustion, char burning rate, and of course also the trajectory of the droplet. Therefore, the location for those burning stages in a furnace is defined by the particle size and shape and the size distribution of the particles. Additional important variables are mass flow distribution and the velocity of the spray. An understanding of spray behavior and droplet

Figure 1. Test series carried out, defined by fluid viscosity and difference from boiling point.

Figure 2. Test series carried out, defined by fluid viscosity and difference from boiling point.

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size and size distribution can be utilized to optimize boiler operation. Naturally, droplet size, shape, and velocity are a part of the input data to computational fluid dynamics (CFD) models and the basis for the study of experimental single particle combustion.

Bennington & Kerekes (1985) were the first to systematically study black liquor spraying with droplet size measurements. They studied laboratory scale grooved-core nozzles with glycerol/water mixtures, superheated water, and a black liquor of solids content of 56%. The spraying temperatures of black liquor in their experiments were 100 °C, 120 °C, and 135 °C, and the consequent boiling point was estimated to be 112 °C. They suggested that the droplet size could be best predicted based on the black liquor viscosity. No sudden change caused by flashing was found. The distribution of drop sizes was found to be much broader than that of a Newtonian fluid having the same apparent viscosity.

Spiebauer et al. (1989) studied black liquor spraying with two sets of experiments. In the first set, they used black liquor of 53% solids content at room temperature, so the viscosity was 150 mPas. The splash plate nozzle orifice size was 9.5 mm and the droplet size was measured by a laser light diffraction based droplet-size analyzer. The second set was carried out with black liquor of solids contents from 66% to 72%. Temperatures varied from 104 °C to 127 °C. These were typical values of recovery boilers at that time and corresponded to a viscosity range of 29 mPas to 66 mPas. The splash plate nozzles used were 9.5 and 12.7 mm of nozzle-orifice size. The third nozzle was a swirl cone type nozzle with a 12.7 mm exit orifice. Droplet size was measured by an X-ray flash based imaging system. They found that a square root-normal distribution provides very good correlations of black liquor spray distributions. The normalized size distribution was found to be almost independent of nozzle geometry, flow conditions, or fluid parameters.

In Finland, the drop size of black liquor sprays was studied first by Mäntyniemi (1987) at Tampere University of Technology. He studied splash plate nozzles in a small recovery boiler to find better spraying practices. He also measured droplet size distribution for a swirl-cone nozzle by spraying water. Droplet size was measured with a laser diffraction based method.

At the Helsinki University of Technology, Laboratory of Energy Engineering and Environmental Protection, the black liquor spraying research started in 1990. The basis of the starting research was on the earlier experience of drop size measurement with easier fluids like water, oils, and coal-water slurries. Many of these studies were confidential. They enabled the purchase of research instruments and inspired researchers to deepen their understanding of spray studies. It was important to have Finnish boiler manufacturers, Tampella Oy and Ahlström Machinery Oy, and the Finnish Recovery Boiler Committee introduce the needs of industry for spraying studies. They funded the research in co-operation with the Ministry of Trade and Industry.

The first experiments connected to black liquor spraying were carried out with small-scale splash plate nozzles and substitute fluids in a vertical spray test chamber. Dimensional analysis was used to scale the results to industrial scale nozzles (Palecouski & Kankkunen 1991). The equations for scaling laws and droplet size based on the Reynolds and Weber number were presented for the first time for black liquor. The drop size was measured with a laser light scattering based particle size analyzer.

The next phase was to measure the drop size of small scale splash plate nozzles with cold diluted black liquor. Drop size measurements could be carried out with a laser light based system with modified optics using a focal length of 4 m (Kankkunen 1993). However, it was not possible to reliably measure the drop size of hot black liquor because the light was scattered by the temperature gradients in the gas around the particles. An image-analysis based system was therefore developed to measure the drop size of hot diluted black liquor sprays (Kankkunen & Heliöpi 1994). The diameter of the splash plate nozzle in these tests was 2 mm and the measured median droplet size was between 200 µm and 300 µm. An increase of droplet size caused by flashing was detected for the first time, as presented in Figure 3. The boiling point of diluted black liquor was 113 °C, and the dry solids content was 70%.

Later, the image analysis was adapted to measure the drop size of industrial scale splash plate nozzles in a vertical test chamber, as reported by Heliöpi & Kankkunen (1996). The choice of measuring in a vertical test chamber was motivated by two reasons. First, there is no need for spray cutting baffles, and secondly, the lighting system for detecting the sheet breakup mechanism can be easily arranged at the sides of the spray. In a horizontal test chamber, the lighting of the sheet must be arranged below the spray and is liable to contamination.

The next tests were carried out in a horizontal test chamber to enable the most reliable test chamber conditions. Here, the breakup mechanism in a test chamber is as similar as possible to spraying into an operating recovery boiler furnace. The comparison between the breakup mechanism in the test chamber and furnace could be fulfilled with a furnace endoscope. The comparison indicated similarity in most of the cases. This is a sign that the results of drop size measurements in the test chamber can be applied in the furnace calculations as shown by Mikkelainen et al. (2002) & by Kankkunen and Mikkelainen (2003).

Droplet size distribution of a large set of test cases was measured in a vertical test chamber with industrial-scale splash plate nozzles and industrial spraying practices by Kankkunen & Mikkelainen (2003). A large fraction of non-spherical particles in the spray was detected. Non-spherical particles were modified as spherical particles with consequent volume. Four droplet size distribution functions were fitted to the experimental data for particle size distributions. The smallest least-square difference was achieved most often by the square-root distribution function. The median droplet size was between 4 mm and 14 mm, as can be seen in Figure 4.

Figure 3. Droplet size of black liquor at different temperatures (Heliöpi & Kankkunen 1996).

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Figure 4. The effect of the mass flow rate on the mass median diameter.

Loebker & Empie (2001, 2002) carried out a broad study with an effervescent nozzle and a splash plate nozzle. They studied droplet sizes and sheet breakup with a very wide viscosity scale from 100 mPas to 3400 mPas. The measured mass median diameters varied from 2 mm to 7 mm, depending on the gas liquid ratio.

Karami et al. (2013) measured the droplet size of small-scale splash plate nozzle spraying water and an industrial-scale nozzle spraying black liquor. They developed equations for droplet size prediction for substitute fluids with small-scale nozzles. The Sauter mean diameter is predicted by the equation

\[ D_{32}=677d^{0.36}V^{-0.35}\mu^{0.003} \]  

where \( d \) is nozzle diameter, \( V \) is velocity, and \( \mu \) is the viscosity of the liquid.

In the case of the flashing liquid, the median droplet size could be predicted by the equation

\[ D_{\text{max}}=1000d^{0.85}V^{0.55}\mu^{0.011}\text{Ja}^{12.6}0.35 \]

where \( \text{Ja} \) is the Jacob number. The Jacob number is defined by equation

\[ \text{Ja}=\frac{\rho G}{\eta h_f} \]
where \( \rho_l \) is liquid density, \( \rho_g \) is vapor density, \( C_p \) is liquid heat capacity, \( AT \) is excess temperature, and \( h_l \) is latent heat of evaporation. Equation (2) is based on a case of a splash plate nozzle with an open exit and a diameter of 27 mm and is sensitive to changes in spraying practice.

**Mass flow rate**

The total black liquor mass flow rate to the furnace is defined by the pulping process. The number, size, and geometry of nozzles can be chosen by operators. The easiest way to control the mass flow rate is carried out by pressure control. Flow control is an essential variable to achieve better combustion and controlled char bed processes.

Spielbauer & Adams (1990) studied experimentally spraying with two splash plate nozzles (9.5 mm and 12.9 mm), v-type and u-type nozzles. The test fluid was low solids black liquors and corn syrup. They concluded that the flow rate could be predicted by a correlation equation based on the Reynolds number and the fluid pressure for all nozzle types. The flow rate was concluded to be insensitive to fluctuations in black liquor viscosity, solids content, and temperature.

The mass flow rate in a nozzle is defined by the following equation

\[
m = C_d A_s \sqrt{2 \rho g \Delta p}
\]

(4)

where \( A_s \) is the area of the pipe cross-section, \( C_d \) is the discharge coefficient, \( \rho \) is the density of black liquor, and \( \Delta p \) is the available pressure difference.

Spielbauer & Adams (1990) experimentally studied Babcock & Wilcox splash plate nozzles. They suggested an equation in the form of the discharge coefficient

\[
C_d = \frac{1}{\sqrt{K_1 + K_2 Re^n}}
\]

(5)

where the constants \( K_1, K_2, \) and \( n \) are obtained by regression analysis. This type of equation can be adapted for conditions below the boiling point. The same form of equation was used by Empie et al. (1995) for three splash plate nozzles. Helpiö & Kankkunen (1995) studied two splash plate nozzle types used by Finnish boiler manufacturers, and they were able to obtain experimental values for the constants. Values for the constants based on these three test series are presented in Table 1. It should be taken into account that in different test series, the pressure difference \( \Delta p \) was measured at different locations.

### Table 1. Discharge coefficient constants based on three test series.

<table>
<thead>
<tr>
<th></th>
<th>( K_1 )</th>
<th>( K_2 )</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spielbauer and Adams</td>
<td>1.17</td>
<td>373</td>
<td>-0.92</td>
</tr>
<tr>
<td>Empie et al.</td>
<td>1.24</td>
<td>458</td>
<td>-0.9</td>
</tr>
<tr>
<td>Helpiö and Kankkunen</td>
<td>-0.04</td>
<td>671</td>
<td>-0.73</td>
</tr>
</tbody>
</table>

Nozzle pressure defines mass flow rate through a splash plate nozzle. An example for a non-flashing case is presented in Figure 5 for three nozzle sizes. The dry solids content of black liquor is 70% (BBR 13 °C).

**Figure 5. Mass flow rate defined by pressure at a temperature of 113 °C. DS 70%, and boiling point of 113 °C (Kankkunen 1996).**

At constant pressure, the mass flow is decreased by flashing, as shown in Figure 6. The inner diameter splash plate nozzle is 15 mm. Pressure difference is 0.9 bar, 1.1 bar, and 1.4 bar (Kankkunen 1996).

**Figure 6. Mass flow rate defined by black liquor temperature for a splash plate nozzle (Kankkunen 2006).**

**Velocity of the spray**

The velocity of black liquor has many important effects on spray properties. At first, it defines the sheet break-up mechanism of the black liquor and essentially affects the droplet size. Next, it defines the spray pattern, spray direction, and locations where droplets hit the char bed or furnace walls. In addition to these, it affects heat and mass transfer processes around particles and the time available for drying and devolatilization.

Spray velocity was first based only on the calculated values, e.g., Empie (1995). Spray velocity was first measured by Helpiö & Kankkunen (1994). They used an image analysis based triple exposure method. They found that the spray velocity increased when the black liquor temperature increased, as can be seen in Figure 7.

**Figure 7. Mass flow rate defined by black liquor temperature for a splash plate nozzle (Kankkunen 1996).**

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**Figure 7. Spray center line velocity as a function of temperature (15 mm nozzle, \( \Delta p=0.75 \) bar) (Helpiö and Kankkunen 1994).**

The boiling point of black liquor was 112.8 °C, and their spraying temperatures were above boiling point up to 125 °C. They also found that for splash plate nozzles, the spray velocity at the spray center line was about 1.4 to 1.9 times higher compared to the calculated average pipe flow even for the non-flashing case.

**Table 2.** Vapor velocity at different locations in the nozzle.

<table>
<thead>
<tr>
<th>Nozzle type</th>
<th>Velocity (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray plate</td>
<td>0.3 to 1.5</td>
</tr>
<tr>
<td>Mill scale</td>
<td>1.5 to 2.5</td>
</tr>
</tbody>
</table>

Late black liquor velocity measurements were carried out with small-scale nozzles by Kankkunen et al. (1998) and mill scale nozzles in spray test chamber by Kankkunen & Nieminen (1997) and by Kankkunen & Miikkulainen (2003).

It was suggested that spray would behave differently in the furnace than in the spray test chamber. Therefore a special furnace endoscope was constructed to measure spray velocities in furnaces as presented by Miikkulainen et al. (2004). A set of measurements in recovery boiler furnaces is presented by Miikkulainen et al. (2000, 2002, 2006, 2009). They developed a new way to define spray center line velocity, and the concept of the dimensionless velocity was presented. Dimensionless velocity was defined as the ratio of measured spray velocity and calculated non-flashing velocity through the nozzle outlet. A very useful way to make comparable measurements with different nozzle sizes and spraying practices was by using a flashing map, as presented in Figure 8. In the flashing map, the mass flux is used to normalize different nozzle diameters, and dimensionless velocity is presented on the vertical axis. An important parameter is the difference from the boiling point – the excess temperature (\( AT \)). With the flashing map, the velocity could be predicted rather reliably for a known spraying practice and nozzle geometry.

**Figure 8. A flashing map for splash plate nozzle type A (Miikkulainen et al. 2006).**
Nieminen et al. (1996) measured the spray velocity of splash plate nozzles using an image analysis system. He found that velocity decreased almost linearly from the spray center line to higher spray angles, as can be seen from Figure 9.

Karami et al. (2013) measured the velocity for flashing black liquor, as presented in Figure 10. Experiments were carried out in a spray test chamber. Figure 10 shows the mass distribution for a full-scale splash plate nozzle with non-flashing black liquor and a small-scale splash plate nozzle with a substitute fluid. The mass distribution decreases almost linearly from the spray center line to the highest spray angle.

Figure 10. Spray velocity at spray angles for a splash plate nozzle (Karami et al. 2013).

Mass flow rate distribution

The distribution of mass within the spray affects the penetration of the spray to the formation of the char bed and to the drying and combustion of droplets. The splash plate angle and the shape of the nozzle exit area affect the mass distribution. Also, flashing is assumed to affect the mass flow rate distribution.

Nieminen (1996) measured spray mass distribution in spray angles by a spray collector. Figure 11 shows the mass distribution for a full-scale splash plate nozzle with non-flashing black liquor and a small-scale splash plate nozzle with a substitute fluid. The mass distribution decreases almost linearly from the spray center line to the highest spray angle.

Figure 11. Mass flow rate distribution of a splash plate nozzle (Nieminen 1996).

Spray mass flow rate distribution was also studied by Empie et al. (1997) for a splash plate and V-jet nozzle. They sprayed 55% to 65% solids content black liquor at temperatures below boiling point and measured spray distribution in spray angles by spray patternators. They found that the mass distribution could be estimated by a parabolic function of the angular position, so that the highest mass flow was in the spray center line.

Karami et al. (2013) presented a new method to estimate mass distribution in the spray. The estimation was based on the light intensity variation of the spray images taken in a horizontal spray test chamber. Figure 12 shows the mass distribution in the spray for two conditions. At a lower excess temperature (14.2 °C), the mass flow rate decreases towards the spray edges. At a higher excess temperature (18.5 °C), the mass flow rate to all spray angles is almost constant.

Figure 12. Mass flow rate distribution for two flashing cases (Karami et al. 2013).

Black liquor sheet break-up mechanism

Black liquor forms a sheet when sprayed at temperatures slightly above (<5 °C) or below boiling point. The sheet thickness decreases when the distance to the nozzle increases as the sheet cross-section gets wider. Disturbances in the liquid and aerodynamics drag around the thinning sheet breaks the sheet into ligaments and then to droplets. The thickness of the sheet and corresponding wavelength (i.e., the length between two fracture points) defines the ligament diameter and consequent droplet size.

When the spraying temperature is sufficiently above the boiling point (typically >10 °C), the sheet is not necessarily formed and at least the sheet break-up is affected by bubble formation. A high temperature in the furnace may dry the surface of the sheet and therefore affect the break-up process.

Bousfield (1990) made an interesting test serial producing a coherent jet with low solids content black liquor. The jet was introduced inside and came out of tubular furnace at temperatures of 950 °C and 1110 °C. He studied the break-up length of the black liquor jet. He found that the length of the jet was decreased for black liquor at room temperature. In the case where the black liquor temperature was 108 °C, the jet length was increased by the hot furnace. He concluded that the viscosity was increased by the drying of the surface of the jet when the black liquor temperature was near its boiling point.

Kankkunen & Nieminen (1997) and Kankkunen (1998) studied black liquor sheet break-up mechanisms. They found three mechanisms. Below the boiling point, the main break-up mechanism was a wavy break-up. Around 5 °C above the boiling point, the break-up was caused by sheet perforations. Around 15 °C above the boiling point, the break-up was caused by high velocity and boiling. The configuration of splash plate nozzles seemed to affect the break-up mechanism, and a combination of break-up mechanisms was detected.

Miikulainen (2006) systematically studied the length and break-up mechanisms of black liquor sheets. He found decreasing length at increasing temperature when the mass flow rate was constant. He also measured the wavelength of a black liquor sheet by image analysis based methods. Experiments were carried out at temperatures from 14 °C to 18 °C above the boiling point.

Figure 13. Sheet break-up mechanisms, wave formation, perforation, and flash break-up (Kankkunen 1998).
Karami et al. (2013) found four different break-up regions for splash plate nozzles. The closed rim break-up mechanism is applicable for small flow rates. In the open rim break-up mechanism, the liquid sheet is continuous until it starts to oscillate and break up into ligaments and droplets. The perforated sheet break-up mechanism produces a sheet that is perforated by flashing vapor bubbles. In fully shattered spray, there is no sheet, but a large number of bubbles and a high velocity at the nozzle exit disintegrates black liquor directly into droplets. Figure 14 shows different break-up mechanisms defined by the Reynolds number and the Jacob number. The secondary break-up of droplets does not seem to be important. Velocities are low – below 15 m/s. Although droplet size is high, secondary atomization is unlikely because of the low velocity and high viscosity of black liquor, as found by Kankkunen & Miikkulainen (2003).

Sprays in the furnace

The purpose of all experiments and theoretical calculations is to predict phenomena and processes taking place in the furnace. Spray properties in the furnace are not necessarily similar as in a spray test chamber. Gas flows in the furnace and heat conduction and radiation may change spray properties. Therefore, experimental studies in the furnace are needed.

Sprays in the furnace have been studied by Miikkulainen et al. (2009) with a furnace endoscope. He could study the spray velocity, sheet length, and breakup mechanism. With another endoscope, Kankkunen et al. (2011) studied spray dimensions and velocities at the distance of 2.3 meters from the nozzle by spraying along the furnace wall. Imaging took place by empty nozzle gun ports. A decrease in the droplet velocity was detected. A part of the images was showing hollow or exploded droplets, which was explained as being caused by excess steam vaporizing from the black liquor. An example is presented in Figure 15. Later, Engblom et al. (2013) showed by CFD simulations that the velocity decrease could be predicted by the decreased density of droplets.

Overall spray studies in the furnace was carried out by Brink et al. (2009). They could see spray directions and opening angles by IR camera.

Figure 14. Spray patterns at different Reynolds and Jacob numbers (Karami et al. 2013).

Computational spray modeling

Nozzles can be simulated by computational methods. Foustä et al. (2002) used the volume of fluid (VOF) model to simulate flow through the splash plate nozzle up to initial sheet breakup and droplet formation. The VOF model solves the conservation equations of volume fraction and momentum utilizing the finite volume technique. The results obtained by the model were different compared to the experimental part of their work. They concluded that the coarse mesh and insufficient computational power hindered reliable results.

Fard et al. (2007) developed a 3D numerical model of free surface flows with an Eulerian fixed-grid algorithm that utilized a volume tracking approach to track fluid deformation. The governing flow equations were assuming an incompressible, Newtonian, and laminar flow. A 3D fixed-grid Eulerian method was written specifically for free surface flows with surface tension. Calculation results of the code, BISpray, were compared to a set with water sprayed to the perpendicular splash plate and to a set where corn syrup was sprayed with a typical 11.9 mm splash plate nozzle. The results were highly similar in predicting spray velocity, sheet thickness, and break-up mechanisms, and even droplet size. The code was used to simulate a new nozzle type that was developed.

Sarchami et al. (2010) at Toronto University used KIVA code to simulate the sheet break-up of a splash plate nozzle. They predicted the droplet size for water sprays produced by 1 mm and 2 mm splash plate nozzles. The predicted droplet size was found to be similar to the experiments.

Järvinen et al. (2006) started a computational analysis of flashing nozzle flow based on the earlier black liquor droplet combustion model (2002). They developed a new model for the growth of a single vapor bubble during flash evaporation of highly viscous liquids. The model consisted of the simultaneous solution of the heat transfer equation combined with the generalized Rayleigh equation for bubble growth dynamics. A simplified thermodynamic, Raoult law based equilibrium model described the vapor pressure of water in a multi-component solution. By using the new model, unit processes during flashing could be studied and understood. It was found that when viscosity increased to values close to black liquor, the initial stages of bubble growth were controlled by viscous and surface tension forces. As the bubble continued to grow further, heat transfer to the bubble surface became the dominating mechanism. The role of the mass transfer of water in black liquor was not studied in detail. When water is removed from the surface, new water should be transported to the evaporation surface to maintain the rate. Järvinen et al. (2006) assumed that as a new surface is constantly created, water is also transported by the radial convection mechanism. The role of water diffusion to the drying front should be better understood and further studied.

Later, Järvinen et al. (2011) used this understanding of the bubble growth for a new computational flow model for a flashing black liquor gun. The model was based on the numerical solution of one-dimensional conservation equations of mass, momentum, energy, steam mass fraction, and bubble number density.

Mass-momentum coupling was solved by the SIMPLE method. Scalar equations were solved by the fully implicit control volume method. Using experimentally measured spray velocities, the model could predict the spray velocity of flashing liquid for a flashing black liquor gun. The initial bubble nuclei concentration in bulk black liquor was found to be an important variable without reliable estimation. The estimation could be obtained from experimental spray velocity measurements.

Computational combustion modeling

Adapting the data in CFD takes the most advantageous part of the initial data produced by experimental sprays studies and spray modeling. Most calculations are based on the Fluent program.

CFD is an important tool for furnace design and engineering. The accuracy of simulations has improved with increased computational capabilities and especially with the increased understanding of flow, heat transfer, and chemical reactions taking place in the furnace. Special emphasis is on the increased understanding achieved by the single droplet experiments by Hupa et al. (1987) and the single droplet combustion model by Järvinen (2002).

Working in co-operation with groups using CFD for furnace simulations is important for experimental spray studies. This has enabled an increased understanding of phenomena affecting furnace operations by spraying. The co-operation with Aalto University and Åbo Academy University has been an excellent example of this.

Conclusions and future directions

The droplet size in a non-flashing case is rather well understood. In the case of flashing spray, the droplet size is difficult to define. The spray velocity is first increased by flashing inside the nozzle. After that, nozzle droplets are exploded by the excess steam coming out from the droplets. Experimental studies carried out for sprays in the normally operating furnace should give a better understanding of a droplet’s fate in the furnace.
The work for a better nozzle flow model for flashing black liquors is actively going on. A one-dimensional plug-flow model was presented by Järvinen et al. (2011). This new model uses measured non-Newtonian properties of black liquor. The validation results of firing pressure, flow rate, and velocity predictions are promising. In the future, the model can be used to develop better spraying practices and nozzles in co-operation with CFD simulations. An important part of improvement in the combustion and recovery process is a better understanding of spray properties, especially droplet size affected by flashing.

New measurement technologies connected to a better understanding of spray behavior and drying and combustion process enable better on-line process control. The lifetime of a nozzle in the harsh furnace environment is normally not an issue after proper material selections and spraying practice have been carried out.

Black liquors are changing in the future, when side flows like lignin, tall oil, and others are utilized. The changes will affect the behavior of black liquors in the nozzle and during the drying and combustion phases. The effect of these changes must be measured and modeled to achieve better furnace control strategies.

References

4. Engblom, M., Brink, A., Hupa, M., Kankkunen, A., Järvinen, M., 2013, CFD Droplet Boundary Conditions from Black Liquor Spray Experiments. 8th International Black Liquor-Colloquium / Black Liquor and Biomass to Bioenergy and Biofuels, UFMG, Belo Horizonte, Brazil.
The accumulation of fireside deposits on heat transfer tube surfaces is a persistent problem in many kraft recovery boilers. The severity of the problem depends mainly on the amount and the melting behaviour of fly ash particles (carryover and fume) entrained in the flue gas, and the efficacy of the deposit cleaning system that the individual boiler employs (Tran 1997, 2004). If left unattended, deposits may form a thick insulation coating on the tube surface, significantly reducing the boiler thermal performance and steam production capacity. In severe cases, deposits may completely plug the flue gas passes, leading to costly unscheduled boiler shutdowns for cleaning. They might also fall, and if large enough, damage screen tubes and floor tubes directly below (Villarroel et al. 2005).

Sootblowers are the principal means of cleaning deposits in recovery boilers. During boiler operation, sootblowers blast deposits off tube surfaces with high pressure steam (Figure 1), while during boiler outages, they use hot water instead of steam to remove the deposits and clean the boiler tubes. Maintaining a high deposit removal efficiency and availability of sootblowers is of vital importance in recovery boiler operation (Chapel 1987, Barsin 1992).

Over the last three decades, much research and development has been done on deposit removal and sootblowing technology by researchers at the University of Toronto, and by researchers and engineers at recovery boiler and sootblower manufacturers. This includes jet hydrodynamics and nozzle design (Jameel et al. 1994, 1996, Moskal et al. 1993), interactions between a jet and tubes and between a jet and deposits (Kaliazine et al. 1997, 1999, Tandra et al. 2007), and the mechanisms of deposit breakup and removal by a jet (Pophali et al. 2009, 2013). The work was carried out through laboratory experiments, mathematical modeling and computational fluid dynamic (CFD) modeling (Emami et al. 2010, 2012), as well as through mill trials (Moskal et al. 1993, Saviharju et al. 2011, Tran et al. 2012). The results provided significant insight into how a sootblower jet strikes and removes deposits from the tube surface, and factors influencing the removal efficiency. These research and development efforts resulted in two major innovations. One is the fully-expanded sootblower jet concept (Jameel et al. 1994, 1996) which served as the basis for the development of the new generation of high intensity sootblower nozzles on the market today (Clyde Bergemann 2012,
sootblowers that can deliver stronger and better controlled jets.

This paper reviews the history of recovery boiler sootblowers, and several important technological advances that have been made in the past three decades.

The history

The word “soot” refers to black, carbonaceous fine particles that are formed during the combustion of coal, wood, oil, etc. Soot forms deposits on the walls of the combustors, chimney and pipes that convey the flue gas. In the context of recovery boilers, soot is synonymous with carryover/fume deposits. A sootblower is simply a device which is used for blowing and removing deposits from tube surfaces.

The first sootblower for on-line deposit cleaning was patented and first used in coal-fired boilers by Diamond Power in 1903 (Barsin 1992). The technology evolved slowly but eventually found its way to other applications including recovery boilers.

In the early days, recovery boilers were designed with close tube spacings that were difficult to keep open. Hand lancing was carried out frequently to remove deposits but was only able to keep the boiler in operation for a short period of time (Chapel 1987). As the boiler became plugged, the operators stopped the liquor firing, opened the boiler mandoors to locate the deposits, and used a long steel rod (or lance) to manually knock them off the tubes. Hand lancing could only handle deposits that were close to the boiler wall. For deposits that were far from the boiler wall or were obscured by tubes/other deposits, hand lancing was difficult as the steel rod needed to be extended deeper into the boiler. For deposits that were behind tubes, it was even more difficult since the steel rod needed to be bent in order to reach the deposits. Hand lancing was dangerous to carry out during boiler operation due to the constant puffing of hot flue gas from the boiler, particularly when the boiler became plugged.

Hand lancing and hand blowing were laborious and useful only for small boilers. As the boiler size increased, these manual cleaning devices became obsolete and were replaced by retractable sootblowers. When the sootblower is not in use, the nozzle at the end of each lance tube reduces the steam flow rate as well as to balance the environment in the boiler. In order to maximize the jet cleaning power as well as to balance the lance tube, retractable sootblowers are equipped with only two opposing nozzles at the tip of the lance tube.

Retractable sootblowers

Retractable sootblowers were developed to address the shortcomings of stationary rotary sootblowers. When the sootblower is not in use, the lance tube is fully retracted and parked outside the boiler, and thus is not exposed to the hostile environment in the boiler. In order to maximize the jet cleaning power as well as to balance the lance tube, retractable sootblowers are equipped with only two opposing nozzles at the tip of the lance tube.

Retractable sootblowers were introduced to recovery boilers in the 1940s; this significant development made large recovery boiler design practical (STEAM 2005). Early retractable sootblowers had a chain drive system that moved and rotated the lance tube in and out of the boiler. The chain was driven by a stationary motor mounted on top of the sootblower canopy (Figure 4). Safety and reli-

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ability were the main concerns for this version of retractable sootblowers. The chain system required constant maintenance. If it failed and broke during sootblower operation, the high pressure steam in the lance tube would cause the tube to torpedo forward and strike the boiler wall on the opposite side at a high speed. This could cause severe damage to the wall tubes and injuries to mill personnel who happened to be nearby.

Modern retractable sootblowers replaced the stationary motor and chain system in the early version to a traveling motor with dual-rack and pinion drives. With such an arrangement, the motor travels together with the carriage as the lance tube is pushed in and retracted from the boiler. The dual-rack and pinion drives have greatly improved the reliability of the lance tube movement. This retractable sootblower design is currently used by the two major sootblower manufacturers, Clyde Bergemann (Figure 5) and Diamond Power (Figure 6).

A schematic of multiple retractable sootblowers installed in a modern recovery boiler is shown in Figure 7. The number of such sootblowers may range from 60 in a small unit to as many as 150 in a large unit.

**Technological advances**

Up to the early 1990s, most improvements made on sootblowing technology were limited to the design and mechanical aspects of the equipment; little attention was given to optimizing the sootblower cleaning power, the steam usage and deposit control strategies. The sootblowing technology used in recovery boilers was literally the same as that used in coal-fired boilers.

In 1991, with the support of 11 pulp and paper related companies and the Ontario University Research Incentive Fund, an industry-university collaborative research program on “Recovery Boiler Fireside Deposits” was initiated at the University of Toronto. The research program included, for the first time, projects on sootblower jet fundamentals and issues related to deposit removal in recovery boilers. The results of this research program, and of programs that followed over the subsequent two decades, and the work of recovery boiler and sootblower manufacturers, have significantly advanced the basic knowledge of sootblowing: how a sootblower jet behaves, how it interacts with tubes and deposits, and identification of the key parameters that influence the deposit removal efficiency. Two important innovations that resulted are fully-expanded nozzles, and low pressure sootblowing technology.

**Fully-expanded nozzles**

The design of sootblower nozzles used in industrial boilers until the mid 1990s ranged from two simple holes drilled into the lance tube to a more sophisticated venturi type, known conventionally as High performance Peak Impact Pressure (Hi-PIP) nozzles (Figure 8a). Hi-PIP nozzles were the most commonly used nozzles in recovery boilers from the mid 1980s to the mid 1990s.

The ability of a sootblower to remove deposits is directly proportional to the jet energy, which is closely related to the peak impact pressure (PIP) of the jet. PIP depends greatly on the steam pressure in the lance tube and the design of the nozzle through which the steam jet passes. By examining the hydrodynamics of a jet passing through a convergent-divergent section of a Hi-PIP nozzle, Jameel et al. (1994, 1996) showed that the jet at the nozzle throat is supersonic. As the jet passes beyond the nozzle throat, it expands and accelerates to a velocity well above the speed of sound, while its pressure decreases in a manner controlled by the shape of the divergent section of the nozzle. Because of the short distance between the throat and the nozzle exit, the jet pressure cannot adjust to the ambient pressure; it is then “under-expanded”, and must complete its expansion outside the nozzle through a series of shock waves. This means that a substantial fraction of the energy available in the steam jet is dissipated as the jet passes through the shock waves, and only a fraction of the initial jet energy is delivered to heat transfer surfaces for cleaning.

Jameel et al. (1994, 1996) also showed that with under-expanded nozzles, increasing the upstream steam pressure above the nozzle design condition only results in a small increase in jet PIP, due to the formation of a larger shock wave. By extending the nozzle length and redesigning the nozzle contour (Figure 8b) to allow the steam to expand fully before it leaves the nozzle, the shock waves can be substantially minimized, and this can greatly improve the sootblower performance. As shown in Figure 9, for the same steam consumption, fully expanded nozzles provide much greater cleaning power than under-expanded nozzles (Jameel et al. 1996, Kalianzine et al. 1997, Moskal et al. 1993).
This discovery led to the development of a new generation of sootblower nozzles that allow the jet to achieve full (or close-to-full) expansion before it exits the nozzle. With the help of CFD modeling and efforts made by sootblower manufacturers, the dimension, shape, and position of the nozzles around the tip of the lance were refined to make it easier for the stream to pass through the nozzles, thereby increasing the cleaning power of the steam jets even further. Figure 10 shows the most advanced nozzles presently offered by the two major sootblower manufacturers: the Diamond Power Gemini nozzles (Diamond Power 2007, Habib et al. 2006) and the Clyde Bergemann CFE (Contoured Fully Expanded) nozzles (Clyde Bergemann 2012, Jameel 1996).

Sootblowing steam is typically taken directly from the final superheater steam outlet and is passed through a poppet valve to reduce the pressure to 7 to 24 bar before entering the sootblower feed tube. Since sootblowers consume 3 to 12% of the total superheated steam produced by the boiler, sootblowing with high pressure steam can be a costly operation. If sootblowers were to operate at a lower pressure, for instance 9 to 14 bar, there would be a significant economic advantage to pulp mills. This is because low pressure steam is less valuable than high pressure steam, as it can be taken from the steam turbine exit after the steam has been used to generate electricity (Figure 12).

The concept of low pressure sootblowing was first introduced to us by a mill representative during our annual research review meeting at the University of Toronto in 2001. Theoretical analysis, laboratory studies and mill trials (Kaliazine et al. 2006, Tandra et al. 2005, 2008, Tavares & Youssef 2006, Tran et al. 2008) were subsequently performed to evaluate the feasibility of the concept. The results clearly indicated that low pressure sootblowing is technically and practically feasible. However, in order for low pressure sootblowers to provide a deposit cleaning power that is comparable to that of high pressure sootblowers, they require a larger jet (a higher steam flow rate) to compensate for the adverse effect of reduced pressure. This can be accomplished by using larger fully-expanded nozzles with a modified design to achieve optimum performance at the lower pressure.

The economic benefits of implementing low-pressure sootblowing technology depend greatly on the amount of additional low pressure steam required to make up for the low pressure, in order to attain the same deposit cleaning power as high pressure sootblowers, and the differential cost between high pressure steam and low pressure steam (Tran et al. 2008). Furthermore, the technology is difficult to implement on existing recovery boilers due to the need for re-piping the sootblowing steam lines to accommodate the higher steam flow rate. For new recovery boilers, this is not an issue, as sootblowing steam lines can be properly designed and installed from scratch. Presently there are three recovery boilers in the United States and two in Brazil using low pressure sootblowers. A few other new recovery boilers are expected to follow suit.

**Sootblower jet strength**

In 2007, a collaborative project was initiated by Andritz Inc., in collaboration with the University of Toronto, Diamond Power and Clyde Bergemann, to systematically examine the strength of sootblower jets in-situ, using a jet force measurement system (Saviharju et al. 2011, Tran et al. 2012). Four trials were conducted under various sootblowing conditions in recovery boilers at two different kraft pulp mills. The main conclusions were that the jet force increases linearly with an increase in lance pressure (Figure 13). At a given lance pressure, the jet force diminishes markedly with an increase in distance from the nozzle. At a distance farther than 1 m from the nozzle, the jet exerts only 10% of its original force on the same target (Figure 14). At greater distances, the jet strikes the target not only with a weaker force but also for a shorter period of time.

The angle at which the jet hits the target also has an impact on jet force (Tran et al. 2012). For a given projected area of the target, the larger the impact angle (closer to the normal direction), the greater is the jet force, i.e. \( F_\text{a} = F_\text{n} \times \cos(\theta) \), where \( F_\text{n} \) is the jet force exerted on the target at \( \theta = 90^\circ \), and \( F_\text{a} \) is the jet force at \( \theta = 90^\circ \) (head-on).
Sootblower Dimension

Presently, there are only a few old and small recovery boilers in operation that have sootblowers mounted on one sidewall, with lance tubes that extend across the boiler width, 8 to 10 m, to the other side wall, in order to achieve full coverage. In most recovery boilers, sootblowers are mounted on both sidewalls so that they need to reach only half of the boiler width. Since the lance tube rests at about 6” outside the boiler when it is fully retracted, the travel length (or distance) is slightly greater than 1/2 of the boiler width.

Prior to 1990, recovery boilers were relative small with a firing capacity under 2500 tds/d. Sootblowers were equipped with an 3.5” OD lance tube and had a travel distance of 5 m. As boilers become larger and larger in recent years, larger 4” OD sootblowers have been used to support a longer lance tube, as well as to accommodate longer fully-expanded nozzles better. Figure 15 shows the sootblower travel length (L) versus boiler firing capacity (F) for a few selected recovery boilers (actual data points). Since most boilers are designed such that the total heat input to the boiler per unit furnace floor area is constant, roughly under 3.3 MW/m², L is proportional to the square root of F (broken curve).

The world’s largest recovery boiler to be built at the pulp mill in OKI, Indonesia will be equipped with 5” OD and 11.6 m long sootblowers. While they will be the largest and longest sootblowers ever installed in recovery boilers, sootblowers of this size are rather common in utility boilers.

Sootblowing Efficiency

Flue gas pressure drop (draft loss) across individual heat transfer banks, attemperator flow rate (% valve opening), steam production rate, boiler bank exit gas temperature, ID fan speed, etc. have traditionally been used to indicate the state of cleanliness (or fouling) of recovery boilers, and to decide when to operate the sootblowers more intensively in the heavy buildup area. While these operating variables provide some indications of boiler fouling, they are not accurate, and often are influenced by other boiler operating variables.

In the early days, sootblowers were operated manually by pushing a button beside each sootblower or in the recovery boiler control room. Based on the experience and logic developed at the mill over the years, the blowing sequence and frequency were programmed into the mill programmable logic controller (PLC) and distributed control system (DCS), which automatically operate the sootblowers “blindly” without any feedback on the state of fouling or boiler cleanliness. In recent years, thanks to the availability of high speed microprocessors and data acquisition systems, several intelligent/smart sootblowing systems have been developed. These systems use more reliable fouling indicators to advise boiler operators when and where to activate the sootblowers, and to optimize sootblowing operation. These include:

- **Heat balance**: This involves the use of a fouling index based on the steam side heat balance performed on each individual superheater section (i.e. primary, secondary and tertiary superheaters), boiler bank and economizer, and the gas side temperatures (Tandra et al. 2010, Ulofth et al. 1996). The fouling index is essentially a measure of the efficiency of a tube bank to transfer heat from the flue gas to the steam flowing inside the tubes. Thus, it can also serve as a key indicator of the sootblowing effectiveness.

- **Strain gauge system**: This system was patented by International Paper (IP) (Jones 2001) and has been installed exclusively in recovery boilers at IP mills. It uses strange gauges installed on the hanger rods that support superheater platen to measure the elongation of the rods, which is directly proportional to the weight of the deposit buildup on the platen.

- **Local deposition rate**: This system analyzes the instantaneous fluctuations of flue gas temperatures at the boiler bank exit during single strokes of all sootblowers in the boiler, and converts them into a time series of raw data that indicates fouling of the tube surfaces (Adams 2010). This, in turn, can be used to indicate the short-term carryover deposition rate and the efficiency of deposit removal by the sootblowers. This approach yields a 3-D map of the local fouling rate in the vicinity of each sootblower that is useful in establishing the sootblowing sequence for minimum steam use or for plugging prevention.

- **Principle component analysis (PCA)**: This system uses a multivariate statistical program to monitor the gradual and sudden shifts in boiler thermal efficiency for individual runs, allowing day-to-day analysis of changes in boiler fouling conditions (Versteeg & Tran 2009).

**Inspection cameras**

The availability of compact, high quality and inexpensive infrared inspection cameras in recent years has enabled mills to inspect the state of deposit buildup at different locations in the boiler during operation, as well as to assess the deposit removal efficiency of sootblowers. Figure 16 shows images of a piece of deposit being knocked off by a sootblower blowing from behind the tube, while Figure 17 shows little evidence of deposit removal by a sootblower in a different recovery boiler as the sootblower moves in and out of the boiler.

Inspection cameras have also helped identify 1) the swinging of sootblower lances caused by the imbalance of jet forces exiting the two opposing nozzles at the tip of the lance tube, ii) locations where massive deposits buildup in the boiler, iii) the cleanliness of the tube surface after thermal shedding events, iv) the swinging of superheater platen and the vibration of boiler bank tubes caused by sootblowing.

**Future outlook**

Sootblowing is a fairly mature technology, particularly with respect to hardware. With the trend toward operating recovery boilers with fewer and fewer operators in years ahead, it will be a challenge for sootblower manufacturers to provide equipment that is easy to operate and to maintain, e.g. gear boxes and other moving parts can be quickly greased; poppet valves and lance tubes can be easily replaced, etc.

Sootblowing efficiency depends on two factors: i) the force exerted by the jet on the deposit, and ii) the strength/tenacity of the deposit on the tube. The peak impact pressure of the sootblower jet and the resulting force can now be predicted.

![Figure 15. Sootblower travel lengths of selected recovery boilers.](image1)

![Figure 16. Images recorded by an infrared inspection camera showing a deposit being removed by a sootblower from behind.](image2)

![Figure 17. Ineffectiveness of a sootblower in removing massive superheater deposits during a blowing cycle (time=mm:ss).](image3)
accurately based on the nozzle design, stream conditions inside the lance tube, and the distance between the nozzle and the deposits. The deposit strength, however, is not as straightforward to optimize the deposit removal process, unless reliable fouling indicators can be developed to advise boiler operators when and where to activate the sootblowers and to optimize sootblowing operation.

Fully-expanded nozzles will remain the preferred choice. Since the present nozzle designs have been optimized for best performance, these nozzles will be used for years to come. New recovery boilers will likely adopt the low pressure sootblowing technology due to its economic advantage.

We will probably see more research and development work on CFD modeling of jet-tube and jet-deposit interactions in the near future. Application of CFD results will help improve understanding of sootblowing jet behaviors. A basic understanding of sootblower jet behaviors has been provided in the literature, and the latest research and development work on CFD modeling of jet-tube and jet-deposit interactions is discussed in detail in this chapter. It is important to note that the optimization of sootblower design and operation is a complex process that involves multiple factors, including deposit characteristics, boiler design, and operating conditions. Therefore, a comprehensive approach is needed to achieve optimal performance.

**Summary**

Sootblowers are required to keep heat transfer surfaces clean in order to ensure high steam production efficiency and high runnability of recovery boilers. Sootblowing technology used in recovery boilers originated from that used in coal-fired boilers. It started with manual cleaning with hand lancing and hand blowing, and evolved slowly into on-line sootblowing using retractable sootblowers.

Prior to 1991, most improvements to sootblowing technology were limited to the design and mechanical aspects of the equipment. Since then, intensive research and development has focused on sootblowing jet fundamentals and deposit removal in recovery boilers. The results have provided much insight into sootblower jet dynamics, how a sootblower jet interacts with tubes and deposits, and factors influencing its deposit removal efficiency, and led to two important innovations: fully-expanded sootblower nozzles are used in virtually all recovery boilers today, and the low pressure sootblowing technology that has been implemented in several new recovery boilers.

The availability of powerful computing systems, superfast microprocessors and data acquisition systems, and versatile CFD modeling capability in the past two decades has also contributed greatly to the advancement of sootblowing technology. High quality infrared inspection cameras have enabled mills to inspect the deposit buildup conditions in the boiler during operation, and helped identify problems with sootblower lance swinging, and superheater platen and boiler bank tube vibrations.

As the recovery boiler firing capacity and steam parameters have increased markedly in recent years, sootblowers have become larger and longer, and this can present a challenge in terms of both sootblower design and operation.

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Higher steam values, higher dry solid contents in black liquor and mill closure have led to major changes in the flue gas and superheater deposition chemistry in recovery boilers. The effects of these trends on superheater corrosion and materials selection are considered with reference to literature data. There is a wide variety of available superheater materials to choose from. There are even few newer materials that should be considered. The operating conditions and deposit properties must be looked at when material selection is done to ensure operational safety and high availability.

The black liquor recovery boiler has multiple roles in a pulp and paper mill which makes it a critical component of a mill. The black liquor recovery boiler is fired with evaporated black liquor that is the spent cooking liquor from the kraft process. It burns the organic material that is contained in the black liquor to generate high pressure steam and nowadays also increasing amounts of electricity; it regenerates the used chemicals in black liquor, and reduces some waste streams in an environmentally friendly way (Vakkilainen 2005).

The modern black liquor recovery boiler technology originates from 1930s and after that a lot of changes have taken place. The most prominent fact characterizing the development of recovery boilers is that their features have changed rather slowly; when any outage will cost a lot of money, the technology tends to be conservative. Economic reasons and environmental constraints have put pressure to increase the energy efficiency of the recovery boilers and traditionally this is achieved by increasing the steam values i.e. temperature and pressure (Figure 1). The trend to increase electricity generation is forcing to increase steam values further. It is calculated that if the steam pressure and temperature can be increased to 104 bar and 520 °C from typical current values of 80 bar and 480 °C the electricity generation capacity of the recovery boiler plant increases about 7% (Vakkilainen 2004).

A key issue for the recovery boiler, as mentioned earlier, is the high availability need. And when recovery boilers are designed one of the most difficult questions that arise is; what kind of materials should one use for different parts of the recovery boiler. In future this is expected to become even more complicated since the demand to increase steam value increase the corrosion risk especially in the superheaters. When selecting superheater materials one needs to consider several factors (Bruno 1997, 1999). Set design conditions (pressure, temperature, corrosion, erosion) determine the boundary conditions. Tube material mechanical properties (strength) determine the tube thickness. Manufacturing properties (weldability, need for heat treatment) determine the required time to manufacture a piece of heat transfer surface. Cost of material and relevant manufacturing cost give the total cost for heat transfer surface. Often also material
availability (time the material can be delivered for manufacturing) plays a significant role. One should not forget that variation of process values during operation (e.g. temperature spikes, overheating and liquor chemistry) can significantly affect corrosion rate and strength of some materials but not others. And in the case of new materials high temperature aging may cause unexpected failures.

Oxidation

High temperature oxidation occurs when metals are exposed to temperatures above 300 °C in gases containing more than 1 vol-% oxygen. Oxidation resistance depends on operational conditions like temperature, gas composition and moisture level as well as on material composition. Oxidation behaviour is affected by combustion products (e.g. carbon monoxide, carbon dioxide) and generally the oxidation rate in flue gases is higher than that in the air. Respectively studies have shown that oxidation rates in moist environments are higher than in dry environments (Figure 2). Temperature limits for different type boiler materials above which oxidation is excessive for 25-30 service years are presented in Table 1. Oxidation resistance is improved by alloying e.g. with chromium, silicon and aluminum. High temperature oxidation is not normally considered to be a problem in recovery boilers due to moderate steam values.

Table 1. Temperature limits for different type boiler materials above which oxidation rate exceeds 25-30 year service life (French 2014).

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon steel (SA210, SA106)</td>
<td>450</td>
</tr>
<tr>
<td>Carbon steel -1/2Mo (SA209)</td>
<td>480</td>
</tr>
<tr>
<td>Low alloy steel 1-1/4Cr-1/2Mo (T11, P11)</td>
<td>550</td>
</tr>
<tr>
<td>Low alloy steel 2-1/4-1Mo (T22, P22)</td>
<td>580</td>
</tr>
<tr>
<td>Austenitic stainless steel 18Cr-8Ni (304, 321, 347)</td>
<td>700</td>
</tr>
</tbody>
</table>

Sulfidation

Typical deposition conditions prevailing in the superheater area of recovery boilers until late nineties, and still common in most of the operating boilers, have been discussed by various workers in detail (Tran 1997, Hupa et al. 1990, Bruno 1997, see also Mäkipää et al. 2001b). The ash depositing in the superheater area consists of both fume particles and carryover particles. Fume particles are composed largely of alkali sulphates, with lesser amounts of alkali chlorides and alkali carbonates. Carryover particles are, in the main, black-liquor residues. In terms of chemical composition, the greatest difference between carryover particles and fume particles is the higher content of alkali carbonates in carryover particles. Superheater tube deposits ideally consisting of sodium sulphate and sodium carbonate that are mutually soluble in the solid state, may form melts in the temperature range about from 826 to 884 °C and higher. Sodium sulphide in the deposit composition may decrease the first melting point of down to 715 °C. Recovery boiler ash in contact with the tube material is thus normally solid. Superheater tube material wastage rates appreciably less than 0.1 mm/a are typical under optimal conditions.

Significant corrosion risks are associated with the high sulphidity of the black liquor (high value of (S/Na+K)), which might lead, especially when the temperature in the lower furnace is low, to high partial pressures of sulphur oxides (up to 1000–5000 vppm of SO2, 100 vppm of SO3). If the material temperature is high, high partial pressures of sulphur oxides cause sulphidation-oxidation of superheater tubes. The mechanisms of sulphidation-oxidation in recovery boilers are basically the same as in power boilers (Bruno 1997). This mode of corrosion is successfully counteracted by using austenitic stainless steel or composite tubing (Oldestam 1982, Ahlers 1987), and/or by shielding the lower parts of the superheater from direct heat radiation by applying screen tubes in conjunction with the “bullnose”, which is the protruding part of the superheater tubes. The corrosion conditions in question may be modelled in laboratory exposing materials to molten mixtures alkali sulphates, carbonates, sulphides and chlorides. Klöwer and White (1990) found that under deposition of 45% Na2S, 21% Na2CO3, 21% of Na2SO4 and 13% NaCl and at temperatures ranging from 550 to 650 °C austenitic stainless steels and high nickel-high chromium steels suffer corrosion. Silicon containing alloy 45-TM performed best, as may be expected considering the solubility behaviour of silica in the fluidising conditions in question. Proper boiler design and high-solids operation, however, effectively eliminate carry-over corrosion. High solids firing enables good mixing and eventually more complete combustion of black liquor droplets entrained in the flue gas flow. In high solids boilers there seems to be low sulfide content in deposits (Raukola & Haaga 2004).

As a concluding note, high chloride pressures advocating active oxidation may be generated in the presence of a thin molten salt film of complex composition (Mäkipää & Koivisto 1999). This corrosion morphology might relate to operation conditions of a peculiar kind, where alkaline deposit conditions prevail but SO2-pressure in flue gases is at least temporarily high. Then, molten alkali chloride – alkali sulphate film will react vigorously with flue gas atmosphere and protective oxide scales to release chloride, as previously shown in (Karlsson et al. 1990). As far as known, no metallic material including hig molybdenum nickel alloys is completely resistant under such conditions.

As discussed by Bruno (1997) and Ahlers (1987), among others, more favourable corrosion conditions occur in the superheater in boilers operated in the high-solids firing mode. In modern boilers firing high-solids black liquor, temperatures in the lower furnace are high, from which it follows that, under steady-state conditions, relatively low concentrations of SO2 are encountered in the upper furnace. Maximum steam conditions that were reached during seventies and eighties were in the range from 480 to 490 °C. Low alloy steel tubing (10CrMo910) with lower bends made of austenitic stainless steel of type 304 were used with success (Jaakola & Rose 1983). More lately, gradually increasing mill closure leading to enrichment of chloride and potassium...
in the flue gases did put an end to this development. The steam conditions from the high level achieved e.g. in Scandinavia backed down to the range of 430–450 °C.

**Deposits**

Recent trends in Kraft recovery process as well as trends in fuel technology related to produce more electricity using renewable fuels has led to major changes in operation conditions. In specific, there is an increased risk of significant alkali chloride deposition in the superheater area of Kraft recovery and biomass fuelled boilers (Jokiniemi et al. 1996). Depending on the alkali metal volatilisation in the furnace, and sulphur and chlorine contents of the fuel, condensation of vapourised alkali chlorides on flue gas particles or directly on heat transfer surfaces may cause accelerated corrosion in the superheater area. Known deposit corrosion mechanisms include corrosion by solid alkali sulphates or alkali chlorides and molten salt attack by low melting mixtures of alkali sulphates, alkali chlorides and alkali carbonates. Contact of tube surface with molten alkali salts causes rapid corrosion. Active oxidation can affect superheater tubes even at temperatures lower than the first melting temperature (FMT). Therefore operating the recovery boiler without gaseous chlorine at burnout is e.g. in Scandinavia backed down to the range of 430–450 °C. The method does not allow with ease to separate corrosion rates observed in practice in cases, where salt cover and atmosphere goes to reactions, which impoverish corrosive species or increase melting point. Corrosion rates more close to practical ones have been reported to be achievable using so-called crucible-method. This method is rather simple to apply. In a recent variation of the crucible method, metallic specimens have been exposed to flowing flue gas atmosphere as burried in synthetic or real deposit, which may be partially molten at the experimental temperature (Kawahara et al. 1997). Test temperature should be chosen so that the content of melt in the bed is less than about 30% allowing for the gaseous atmosphere an access to the corrosion front, typically leading to test temperatures in the range of 550–560 °C. Specimen cooling may be applied to simulate temperature variation and temperature gradient. Materials evaluation is based on post-experiment examination of specimens and their cross-sections. However, this method does not allow with ease to separate between reactions of solid and liquid phases in the deposits, or to analyse the effect of gas phase composition on the corrosion reactions. Electrochemical measurements in combination with crucible tests are in principle very helpful, but these measurements are too intrusive to be applied widely.

In the study of Oksa and Mäkipää (2001) modified crucible test method was introduced that simulates this corrosion condition. Metallic specimens exposed in air atmosphere as half-immersed into a fully molten alkali chloride - alkali sulphate salt mixture of eutectic composition in 520–530 °C. Materials used in the test were low-alloy steels, stainless steels and nickel alloys: 10CrMo44, 10CrMo910, AISI 304, HRSC, AC166, 45TM, YUS 170 TBM, S–C, Sanicro 28 and Inconel 625. For low-alloy steels and austenitic stainless steels the characteristic corrosion attack mode was intergranular attack and growth of oxide scales. More corrosion resistant steels and alloys suffered from pitting attack. Corrosion morphologies observed had a close resemblance to practical corrosion morphologies in cases involving alkali sulphate - alkali chloride melt attack. Corrosion morphologies, which were obtained in 44 or 65 h testing for low-alloy steels, correspond reasonably well with corrosion morphologies observed for low-alloy steels in various corrosion failure cases, where excessive material wastage has occurred. Short-term exposures give some additional information about the initiation stage of the rapid general material wastage of low-alloy steels and austenitic stainless steels as well. As shown in Figure 3a for 10CrMo910, and in Figure 3b for austenitic stainless steel type AISI 304, deep intergranular attack occurs causing individual grains to detach from the substrate to form individual islands of metal. These results suggest that the ranking of austenitic stainless steels is largely dependent on their relative susceptibility to grain boundary attack. YUS 170 material had endured test well below the melt line. Material surface, which had been above the melt, was covered with small corrosion pits. Thus, steels like YUS 170 without any signs of grain boundary attack in the half-immersion test, should perform better than some other steels of similar composition but prone to grain boundary attack in the test.

Initiation of grain boundary attack may be suppressed under various conditions, basic or acidic, by alloying silicon. Silicon is known to be useful in two ways. Silicon enhances chromium diffusion in the alloy accelerating protective chromium oxide scale formation. On the other hand, silica may form a thin amorphous silica subscale, which is not soluble into alkali sulphate melts, and is practically impermeable to chromium, nickel, chloride etc. Furthermore, it has been claimed by various workers that solubility of silica in sodium chloride melts independently of the melt acidity. Furthermore, it has been noted that it is rather basic fluxing by Na₂O than acid fluxing by SO₃ that is responsible of protective scale dissolution in sodium carbonate- sodium sulphide - sodium sulphate - sodium chloride salt mixtures found on BLRB superheater tubes under carryover conditions (Klöwer & White 1995). Accordingly, various silica forming alloys have been developed for use in superheaters of waste incinerators, and recommended to be used also in high-pressure recovery boilers. Half-immersion tests made put this proposition in some doubt: silicon-containing nickel alloy was found to be susceptible to grain boundary attack on specimen surface areas located above the immersion line (Oksa & Mäkipää 2001). In opposition to the case of alkali-sulphate-chloride-carbonate-sulphide precipitation reactions may take place in thin salt films and, depending on the melt and gas phase composition, may therefore radically change the corrosion potentials and the ranking of various alloys and steels.

High cost of 25% Cr -grade austenitic materials and their tendency to localised corrosion in the presence of alkali chlorides has motivated a number of materials development and testing programmes in North America, Japan and Europe. However, methodologies used for corrosion testing in laboratory or for material exposures in full scale using cooled probes are not uniform. The only standardised hot corrosion test method, which applies thin salt layer covering replenished with relatively regular intervals, does not reproduce corrosion rates observed in practice in cases, where salt cover and atmosphere goes to reactions, which impoverish corrosive species or increase melting point. Corrosion rates more close to practical ones have been reported to be achievable using so-called crucible method. This method is rather simple to apply. In a recent variation of the crucible method, metallic specimens have been exposed to flowing flue gas atmosphere as buried in synthetic or real deposit, which may be partially molten at the experimental temperature (Kawahara et al. 1997). Test temperature should be chosen so that the content of melt in the bed is less than about 30% allowing for the gaseous atmosphere an access to the corrosion front, typically leading to test temperatures in the range of 550–560 °C. Specimen cooling may be applied to simulate temperature variation and temperature gradient. Materials evaluation is based on post-experiment examination of specimens and their cross-sections. However, this method does not allow with ease to separate between reactions of solid and liquid phases in the deposits, or to analyse the effect of gas phase composition on the corrosion reactions. Electrochemical measurements in combination with crucible tests are in principle very helpful, but these measurements are too intrusive to be applied widely.  

**Figure 3. a) Cross-section of 10CrMo910 and b) cross-section of AISI 304 stainless steel after 20 h exposure in eutectic alkali chloride melt (6.5 wt-% NaCl , 59.0 wt-% Na₂SO₄ and 34.5 wt-% KCl) at 525 °C (Oksa & Mäkipää 2001).**  

Sodium and potassium may enhance formation of ash deposits with low melting points 510–600 °C. Minimum melting points in deposits consisting of complex mixtures of alkali and alkaline earth metal salts are in the range of 490–510 °C, which is much lower than 550–575 °C, i.e., material temperatures related to steam values 500–525 °C. In various practical corrosion failure cases one finds that corrosion environment has actually been a low melting salt film spreading on the superheater tube surfaces leading to excessive material wastage in spite of reasonable material temperatures (Mäkipää & Koivistio 1999, Crews & Youngblood 1998, Fujikawa et al. 1999). Complex dissolution pre-
One may consider closed volumes of molten salt film and metal surface in the case of higher alloyed materials (figure 4). for the latter the iron content suffered from serious pitting corrosion at temperatures below 800 °C. Accordingly, some workers exclude active oxidation as an operating corrosion mechanism in recovery boilers, whereas rapid chloride induced low-temperature oxidation corrosion, active oxidation (Spiegel et al. 1997, Reese & Grabke 1993), may occur in fluidised bed at material temperatures which are well below the first melting point of the deposits, then being due to alkali chloride sulphation reactions (Salmenoja & Mäkipää 1999, 2000). It has been found, however, that alkali chlorides induce active oxidation even under SO₂-free atmospheres (Mäkipää et al. 2001b, Hilden et al. 1999, Mäkipää & Fordham 2000, Mäkipää & et al. 2001c, Skrifvars et al. 2008, Lehmusto et al. 2013). Material wastage rates of low alloy steel specimens exposed to alkali chlorides under oxidative atmospheres are excessively high (> 0.1-10 mm/a) starting from temperatures of about 450 °C and depending on the alkali chloride and actual gaseous atmosphere composition and flowing conditions in different corrosion morphologies.

As noted by Keiser et al. (2009) there is, however, seemingly no consensus between various groups on the relative corrosivity of various alkali chlorides and on the critical temperature interval of corrosion reactions. One may write a number of hypothetical corrosion reactions suitable, in principle, also for their experimental verification in laboratory, see Rapp & Grabke et al. (1993), Spiegel et al. (1997), Skrifvars et al. (2008), Lehmusto et al. (2013), among others:

\[
\begin{align*}
Na_2CO_3/2NaCl(s) + FeO(s) + O_2(g) &\rightarrow Na_2FeO_4(s) + CO_2(g) + Cl_2(g) \\
K_2CO_3/2KCl(s) + FeO(s) + O_2(g) &\rightarrow K_2FeO_4(s) + CO_2(g) \\
4K_2CO_3 + 2Cr_2O_3 + 3O_2(g) &\rightarrow 4K_2CrO_4 + 4CO_2(g)
\end{align*}
\]

Validated thermodynamic data do not support the view that alkali chlorides react with iron oxide to from stoichiometric alkali ferrite (Na,K)FeO₃ and gaseous chlorine (Mäkipää & Fordham 2000). Instead, initial formation of various ferrates (of type (Na,K)FeO₄) and various nonstoichiometric gamma-ferrites and polyferrites (i.e. of type (Na,K)Fe₂O₇), accompanied by adsorption of liberated chloride ions on oxide surfaces would be more plausible explanation for experimental findings. Contrary to the case of alkali ferrites, thermodynamics strongly favour formation of alkali chromates, molybdates and manganates as corrosion products under oxidative conditions. Using X-ray diffraction, sodium chromate (Na₂CrO₄) was found in the phase composition of corrosion products detached from cooled probe exposed for 2000 h in recovery boiler superheater area (Mäkipää et al. 2001). The presence of chromate has been reported several times by Japanese workers.

When instead of oxides of the alloying elements their metallic form is considered, affinities of the gross corrosion reactions referred to above are greatly enhanced. Accordingly, metal and alloy specimens prepared using standardised methods, respectively the formers of a very thin oxide (Cr₂O₃) scale only, may be suspected to underperform in laboratory testing or boiler exposures using ground specimens attached in cooled probes, see Figure 5 and Figure 6.

Figure 4. a) Large corrosion pit on the surface and b) cross-section from the bottom of a large corrosion pit (BE-image) on UNS N08028 after 20 h exposure in eutectic alkali chloride melt (6.5 wt-% NaCl, 59.0 wt-% Na₂SO₄ and 34.3 wt-% KCl) at 525 °C (Oksa & Mäkipää 2001).

Note: Selective corrosion of chromium (and iron) and enrichment of nickel (and iron) at the pit bottom.

Figure 5. TGA-curves showing weight gain in various cases. Specimens embedded in NaCl or KCl beds in a Pt crucible. Total exposure time 35 h (Mäkipää et al. 2001a).

One must however, be aware that the affinities of the hypothetical corrosion reactions considered...
above are themselves critically dependent of material temperature and gas phase composition both. Actual, or local, values of $pO_2$ and $pCO$ are highly important parameters in theory, but experimentally hardly controllable. Thus, reaction products formed in corrosion scales may dissociate and form again locally and timely, as well in full-scale as in experimental conditions in laboratory. Alkali metal-, $H_2O^+$, $NH_4^+$ and chloride ions are known to stabilize gamma-iron oxide (maghemite), thus having the potential to affect stress and growth properties of the oxide scale (Aleksander 1963, Davies et al. 1973, Boettger & Umland 1974). Alkali chlorides possess this ability even when present at ppm-level. Exposure to alkali chlorides even temporarily may enhance oxide scale growth (Boettger & Umland 1974, Ross & Umland 1984). Water vapour enhances, and carbon dioxide somewhat reduces alkali chloride aggressiveness (Malkow et al. 2001). Corrosion reaction schemes in simplified theoretic models may fail in practical work. Seemingly contradictory results concerning corrosiveness of sodium and potassium salts as pure or in their mixtures may be obtained by various laboratories as noted before. Experiments using thermal ramps or thermal cycling may result to very different corrosion morphologies as compared to experiments at constant temperature, Figure 7.

In particular, due to the higher thermodynamic stability and to the higher vapour pressure of sodium iron oxide and complex sodium iron chloride, respectively, as compared to the corresponding potassium compounds, metallic specimens of low alloy steels (10CrMo910 and 15Mo3) tend to lose some weight when exposed to sodium chloride whereas they show weight gain and thick multi-layered oxide scales when exposed to potassium chloride, Figure 8. Thermodynamic background of the very complicated corrosion reactions in question is known inadequately, and should be carefully scrutinized. As an example of the usefulness of such exercises for practical corrosion science, the works on vapourised species in the system Cr-O-Cl-H may be referred to (Liu et al. 2009, Jiao et al. 2011, Asteman et al. 2002). See also Figure 5 and Figure 6.

The experimental findings referred to above experimental are in line with earlier results, e.g. with those of Alexander (1963), Davies et al. (1973, Boettger and Umland (1974), and also of Shinata and Nishi (1986). Austenitic stainless steels have been found to suffer from general corrosion attack as exposed to both sodium and potassium chlorides, (Mäkipää et al. 2001b, Mäkipää & Fordham 2000, Malkow et al. 2001), whereas various high chromium alloys corroded only if exposed to potassium chloride. Most resistant in both sodium and potassium chlorides are high-nickel, high-molybdenum alloys of type Alloy 625. This finding is consistent with
The main steam temperature is the main parameter that affects the choice of superheater materials, as this is because the corrosion rate increases as the superheater steam temperature increases. Figure 10. However it should be noted that the superheater corrosion rates are not uniform, but depend strongly on the local conditions. Superheater surface temperature can be tens of degrees higher than the bulk steam temperature, Figure 11. A rough estimate is that in areas where radiation is present the metal temperatures are about 50 °C higher than the steam temperature (LaFond et al. 1992). This is taken into account when positioning superheaters. The corrosion risk of hottest superheaters can be reduced by placing behind the nose or protecting it by screen tubes. Corrosion risk can also be reduced by controlling deposition chemistry and avoiding condensation of potassium chloride i.e. by removing non-process elements (NPE) (potassium and chlorine) from the chemical recovery process (Tuiramo & Salmenjoja 2001, Kaneko et al. 1998, Jaakkola 2009).

**Carbon steel and low alloyed steels**

Carbon steel is only used in the coldest part of the superheaters, their corrosion rates are acceptable if steam temperatures are below 400 °C (corresponding metal temperature 430–450 °C) (Sharp 2007). According to Vakkilainen & Pohjanne, (2010) typical primary superheater materials, when they are protected from direct furnace radiation are carbon steel (SA/A-210 Gr A-1, S235JRG2) which can be used up to 350–400 °C. Secondary and tertiary superheater materials contain often 1-3% Cr to improve corrosion resistance. Examples from these are 13CrMo44, T11/10CrMo5-5 and T22/10CrMo910 which are used up to 400–480 °C. These are characterized by significantly increased strength at elevated temperatures and elevated scaling temperature. However, their corrosion resistance is quite limited and therefore they are useful at temperatures significantly below the FMT (Sharp 2010). Similar guideline is presented in Clement & Grace (2009) where it is mentioned that T22 can be operated at steam temperature of 496 °C if chloride levels are kept low.

**Stainless steels**

Corrosion resistance is increased with chromium alloying and martensitic (X10CrMoVNb9-1, X20CrMoV11-1) and austenitic (X1NiCrMoCu31-27-4, NiCr22Mo2Nb) steels are used in hottest and most corrosive superheaters up to 500–520 °C (Vakkilainen & Pohjanne, 2010). AISI 347 has been widely used in current superheaters typically as short pieces in most corrosive places. Parts manufactured from AISI 347 have no record of corrosion failure in Finland. In high temperature boilers, where improved intergranular corrosion resistance is needed alloys like 309 and 310, with higher amounts of chromium should be used. According to Tuthill (2002) austenitic type 310 stainless steel or more highly alloyed material either as solid or compound tubes is recommended for superheater tubing when the outlet steam temperature exceeds 480 °C.

Nippon Steel & Sumitomo Metal Corporation (NSSMC) is supplying grades HR2M (22Cr14Ni1.5MoN), MN25R (25Cr14Ni0.8 Mo0.3N), HR3C (25Cr20Ni18Nb) and UNS N08028/X1NiCrMoCu31-27 (27Cr31Ni3.5Mo) either as mono or compound tube. Compound tube and the grade X1NiCrMoCu51-27 (27Cr31Ni3.5Mo) is targeted to European market whereas mono tubes are supplied to domestic customers (Nippon 2014). Composite tubes are attractive, because they are not susceptible to steam/water side stress corrosion cracking. The experiences have been mainly positive. In example cases Unifuse 310 welded coating is reported to last more than two years without visible damage. In the same conditions the old steel (T11) corroded 3.9 mm/year (Lai & Blogg 2003).

**High Cr – high Ni – Fe base alloys**

Sanicro 28 (UNS N08028) is currently used in recovery boiler superheaters as compound tube. It has a good corrosion resistance because of high Cr (27%) and Ni (31%) content, other alloying elements being 5.5% Mo and 1% Cu. Sanicro 28 has low carbon content to which also Japanese tube manufacturers are targeting. AC66 (1.4877) is like Sanicro 28, but it doesn’t contain Cu and it is Nb-stabilised because of the higher carbon content. This material has not been widely used in recovery boilers, but in comparable corrosion conditions at biomass boilers it has been proven as one of the best materials. Alternative grades from Nippon Steel & Sumitomo Metal Corporation (NSSMC) are UNS N08825 and HR11N (UNS N06811) (Nippon 2014).

**High Cr – high Mo – Ni base alloys**

Materials belonging to this category are e.g. Sanicro 63, Sanicro 67, Super 625. These high molybdenum grades have excellent service records from waste incineration. When selection these materials special attention should be paid on manufacturing as well as on long-term stability and ageing at high temperatures (Kawahara & Kaihara 2001). WSI has also developed and used Unifuse 52 type welded coating (28% Cr, 14% Fe with minor amounts of Al and Ti) for use in coal fired boilers (Lai & Blogg 2003). Coating can be welded to carbon or austenitic steel tube.

**Conclusions**

Higher steam values, higher dry solid contents in black liquor and mill closure have led to major changes in the flue gas and superheater deposition chemistry in recovery boilers and increased super heater corrosion failures. Following corrosion modes may be present either alone or in combination; 1) molten salt attack, 2) low temperature oxidation / active oxidation and 3) sulfidation under reducing deposit conditions. High sulphidity of the black liquor (high value of S/Na+K), which might lead, especially when the temperature in the lower furnace is low, to a high partial pressure of sulphur. If the material temperature is high or even moderate, high partial pressures of sulphur oxides may cause sulphidation-oxidation of superheater tubes. The mechanisms of sulphidation-oxidation in recovery boilers are basically the same as in power boilers. This mode of corrosion is successfully counteracted by using austenitic stainless steel or composite tubing. Excessive carryover of unburned black liquor droplets may cause conditions in superheater deposits which are locally reducing, and siffs the deposit composition to the one where the melt is rich in alkali sulphides. The melting point might be suppressed to the extent that rapid material wastage occurs. Even polysulphide rich melts may become stable in the salt system in question in presence of elemental carbon, leading to extremely rapid material wastage.

Another typical corrosion problem is molten salt attack, which is most likely to occur when the boiler is operated outside the designed capacity. In reducing flue gas conditions the partial pressures of oxygen and sulphur oxides may be too low, sulphation of alkali chlorides in the furnace is much less, and chloride rich deposits with low melting points may form. Molten phase corrosion can be mitigated by keeping the superheater metal temperatures below the FMT of the deposits. This can be achieved either with correct steam values or by removing NPE (potassium and chlorine) from the chemical recovery process. As known from other fields of boiler technology, alkali chloride rich melts have the potential to cause rapid corrosion even at material temperatures of 400 °C and lower. Low temperature oxidation /active oxidation mechanisms which occur below FMT of the deposits, involving complex volatile corrosion products and low melting mixtures, are not well


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Continuous chemical process industries seek to reduce economic, safety, and environmental losses in order to primarily meet societal demands, governmental regulations, and the competitive market. All of them are increasingly tight. Any information that contributes to at least mitigate such potential losses is desirable. However, large-scale chemical systems are complex by nature. They are multivariable, with non linear relationships and noisy measurements, and are of partial knowledge. In addition, continuous chemical systems are characterized by presenting multiple normal operating modes. This scenario makes its description difficult in practice. Quantitative (purely mathematical) and qualitative (such as expert systems) models are limited in this task, either because of a lack of knowledge or an arduous mathematical description (Venkatasubramanian et al. 2003a,b,c). An alternative approach is getting information directly from data, which is more and more available in chemical industries. Nowadays, with the advance of the informatics, database and industrial instrumentation areas, hundreds and even thousands of process variables, among flow rates, temperatures, pressures, concentrations, and so on, are continuously collected from a multitude of plant sensors and stored until every second (Chiang et al. 2001, Wang, 1999). The resulting databases are called process historical data (PHD) since they carry the history of the operations. Thus, the availability of data is no longer a problem. From a past poor-data world to a current rich-data world, the new challenge is how to transform these massive amounts of raw data into relevant information to be applied in the benefit of the company. In other words, the common lack of data in the past decades has been replaced by the challenge of mining relevant information from massive amounts of data. This new paradigm imposes new questions with regard to data analysis (Venkatasubramanian, 2009). Due to the limitations of both quantitative and qualitative models, in conjunction to the growing availability of process historical data, data-driven models, which are developed directly from the data, have increasingly been employed to transform raw data into useful information. This approach opened a new possibility of directly extracting relevant information from very large data sets. Its use in place of the process-driven concept gains strength every day. Handling and interpreting massive amount of data manually is infeasible in practice, and supporting computational tools are absolutely essential. These tasks become more difficult as the number of process variables increases and the sample time gets lower.

Next section describes the way collected data are usually employed in recovery boilers. In sequence, recent studies making use of new techniques or approaches to transform process historical data into relevant information are illustrated.
Use of process historical data in recovery boilers

The availability of process data collected in recovery boilers increased from the nineties. Nowadays, massive databases are available in every medium or big mill. Like chemical industries, this data is very little explored. Its on-line use is in general limited by monitoring key process variables through univariate trend plots. One drawback of this independent procedure is that the spatial correlation among the variables is not taken into account. Then, a measurement seen as normal may be in fact the onset of an abnormal condition. In addition, this disregard causes distrust of the alarm levels, and in consequence an unsafe operating condition may arise. Another characteristic of process data is the serial correlation. When constructing control charts it is also needful to consider this point mainly in case of low sample times. The off-line use of the stored data is mostly in diagnosis tasks. In general, it is carried out with the aid of scatter plots, which show the relationship between two process variables. However, as a multivariate process with high correlations among variables, diagnosis tasks in recovery boilers would benefit from a simultaneous visualization of a group of process variables. Visualizations based on the orthogonal space (as scatter plots) are limited to a maximum of three variables. By applying attributes such as color, shape, and size, it is feasible to represent about eight dimensions (Cleveland, 1993). Other solutions include subspace selection (i.e. multidimensional reduction) or axis translation by using for example principal component analysis. Both approaches cause loss of information. Then, multidimensional visualizations would be valuable in helping the understanding of recovery boilers’s operations. Another point is related to the definition of a key variable subset with the purpose of monitoring, whose selection is based on process expertise in general. However, in addition to this chosen set of process variables, it may be possible that other relevant variables exist. These variables may be uncovered by investigating the stored process historical data. Subsets of variables may also contain redundant information. By using them to construct data-driven models such characteristic may cause the deterioration of their performances. In brief, as occur in continuous chemical process industries in general, process historical data are still little explored in recovery boilers.

The following studies give examples of utilization of process historical data in recovery boilers. Almeida et al. (2004a) applied variable selection techniques and artificial neural networks to select best variable subsets with respect to steam generation. Almeida et al. (2004b) used data visualization techniques that allowed a visual representation of a set of process variables simultaneously. Versteeg and Tran (2008) and Versteeg et al. (2007) applied principal component analysis and partial squares to analyze the fouling problem in recovery boilers. Major operating variables that caused fouling and plugging were identified with monitoring purpose. Martelli et al. (2008) employed artificial neural networks for detection of incipient defects in control systems. The case study was the secondary air system of a recovery boiler. Examples of graphical analysis using scatter plots and trend plots were given by Porter et al. (2010) and Vakkilainen et al. (2010). The former carried out a data analysis on the black liquor being fed to a recovery boiler, and the latter examined the emissions from a recovery boiler using different time point views. Vakkilainen (2010) also made use of such plots to study the relationship between dust properties and a set of operating variables.

New approaches for use of process historical data in recovery boilers

This section presents a collection of studies conducted by the authors with respect to the use of process historical data in recovery boilers. The data-driven techniques employed belong to the multivariate statistics, computational intelligence, and the signal processing fields. An example of simultaneous multidimensional visualization is also given. The case studies include sensitivity analysis, visual representations, and communication facilities; abnormal situation management; fault detection and diagnosis, and visual analytics; abnormal operating variability detection; and handling of multiple normal operating states, and minimization of false alarm rates. All case studies employ real data collected in recovery boilers from pulp mills in Brazil. The structure of each case study is given by the practical challenge in question, the goal of the application, and the employed data-driven technique, the main obtained results, followed by a brief closing. The title of each section is related to the goal that motivated the study.

Communication facilities

The understanding of massive numerical data bases is not a natural task for human beings. This fact explains in part the growing tendency of representing them in a graphical way. The motivation behind it is the human capacity to process visual information (Marakas, 2002). Graphical representations can be employed to attend explanatory, exploratory, confirmatory, and communication goals.

The following results were presented in Almeida et al. (2008a, 2010). The collected database refers to four months of a recovery boiler operation that belongs to a pulp mill in Brazil. Its operation was considered normal during the whole period. There are eight process variables with about three thousand measurements for each one. The goal was to construct a cause-effect map showing the contribution of this set of process variables to the output steam. This was achieved by performing a sensitivity analysis study. Firstly, a predictive artificial neural network model for the output steam was obtained. This data-driven technique belongs to the computational intelligence field. It was used due to its capacity of accomplishing direct input-output mappings once only process variables were available, as well as dealing with noisy data. Next, the input process variables were disturbed, one at a time, and the output steam measurements collected at the mill compared to the corresponding model outputs. The Mean Squared Error (MSE) metric was used as a measure of this discrepancy (Table 1). The larger it is, the higher the contribution (fourth column of Table 1) of the input variable on the steam generation.

In sequence, a graphical representation of the previous (numerical) results was constructed (Figure 1). The eight input variables were allocated into three groups, namely combustion process heat (QSS), preheated combustion air (QCA), and sensible heat (in the fuel) (QB1). Each one relates to a distinct heat source in the boiler. This segmentation makes the interpretation of the contribution of each group (or each variable in a particular group) on the steam production easier. The map shows arrows from all input variables towards the output steam. Their thicknesses are proportional to the previous results obtained for the MSE values (Table 1), and hence they represent the contributions of the variables over the steam produced by the boiler. The thicker the arrow, the stronger the effect. Block 1 gives the main source of heat (76.9%) in the boiler. In modern recovery boilers, which it was not the case here, it may account for more than 85% of the total heat available. Block 2 answers for the second greater influence on steam generation (23.0%). The contribution of Block 3 is negligible. Figure 2 shows a submap derived from Block 2. It allowed a cleaner visualization of the contribution given by each level of combustion air on the steam generation. It showed the greater effects of the secondary (37.8%) and tertiary (51.7%) levels of air compared to the primary level of air (10.5%), whose focus is on the char bed. The obtained cause-effect strengths are in accordance with the literature (Adams et al. 1997, Vakkilainen, 2005) and common operating practices. The relative magnitude of each effect became more intuitive by using both maps compared to the numerical results (fifth column of Table 1). The higher the number of process variables, the clearer the role visual representations play. The grounded knowledge concerning steam generation by recovery boilers served as a benchmark for validation of the methodology. Having process historical data available, at first it can be applied to any other boiler’s subsystem.

Graphical representations provide a more intuitive understanding of system’s structures. Here numerical results (Table 1) involving nine process variables (eight inputs and one output) were transformed into 2D visual representations (Figures 1 and 2). For instance, they can be useful for knowledge dissemination, decision-making processes such as variable selection, and for leveling when putting together analysts from distinct areas. Visual representations may also give unexpected or new insights into the system.
Abnormal situations can be defined as disturbances that deviate the operations from the normal states. Their causes are the human factor, the process itself, and the equipments. Human factors relate to the lack of procedures, incorrect actions, and noncompliance with instructions. Overloads and mechanical failures are the main sources of abnormal situations with respect to process and equipment disturbances, respectively (ASM, 2005). To prevent or at least mitigate potential losses, automatic and reliable monitoring systems are more and more needed in mill control rooms (PAS, 2000).

A risk situation in recovery boilers refers to the accumulation of ash deposits, mainly composed for sulfur- and sodium-based salts, along its convective heat transfer section. Potential losses in this case refer to the reduction of the steam generation efficiency, the lower disponibility of the boiler due to blockage of the fuel gas path, and the greater maintenance costs. Pulp mills manage it in day-by-day through the use of a set of sootblowers as well as the continuous monitoring of key process variables in the control rooms (Vakkilainen, 2005, Adams et al. 1997).

The following study (Almeida and Park, 2009) constructed a system to monitor the state of the ash deposits over the heat section. The database covers ten months of operation of a recovery boiler at a pulp mill in Brazil, with a sample time of one minute. Five measurements of fuel gas pressure drops (ΔP) across the heat exchangers of the heat section and also the electrostatic precipitator were employed as monitoring variables (Figure 3). The monitoring system was given by a data-driven technique belonging to the signal processing field called hidden Markov model. Every chemical process is under random influences due to an inherent variability. Then, measurements of process variables may be seen as realizations of an underlying stochastic process. This way, specific operating conditions can be described by particular probability distributions (Venkatasubramanian et al. 2003c). This is the motivation for applying the hidden Markov modeling to chemical process monitoring, once it is capable to identify changes of statistical nature in signals (in this case, given by process variables measurements) over time. Its output is a likelihood value (–log[P(O|λ)]), which is a measure of the capacity of the model (with parameter λ) in generating a temporal

<table>
<thead>
<tr>
<th>Disturbed Variable</th>
<th>Symbol</th>
<th>MSE (ton/h)^2</th>
<th>Dev₁ (ton/h)^2</th>
<th>Dev₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black liquor flow rate</td>
<td>Fₘ</td>
<td>551.6</td>
<td>477.4</td>
<td>51.2</td>
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<tr>
<td>Black liquor temperature</td>
<td>Tₘ</td>
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<td>1.0</td>
<td>0.1</td>
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<tr>
<td>Dry solids content</td>
<td>%ₓₛ</td>
<td>313.8</td>
<td>239.6</td>
<td>25.7</td>
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<tr>
<td>Primary air flow rate</td>
<td>Fₚₘ</td>
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<td>15.0</td>
<td>1.6</td>
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<td>Primary air temperature</td>
<td>Tₚₘ</td>
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<td>7.5</td>
<td>0.8</td>
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<td>Secondary air flow rate</td>
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<td>Secondary air temperature</td>
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<td>41.6</td>
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<tr>
<td>Tertiary air flow rate</td>
<td>Fₚₜ</td>
<td>185.2</td>
<td>111.0</td>
<td>11.9</td>
</tr>
<tr>
<td>Total</td>
<td>-</td>
<td>-</td>
<td>932.6</td>
<td>100.0</td>
</tr>
</tbody>
</table>

† Dev₁ (ton/h)^2 = MSE – MSEₛ, where MSEₛ = 74.2 (ton/h)^2.
‡ Dev₂ (%) = (Dev₁/Total Dev)•100, where Total Dev = 932.6 (ton/h)^2.
sequence of data (o) continuously made available over time (Rabiner, 1989). For instance, a hidden Markov model characteristic of normal operating conditions can be used to detect deviations from it (caused by disturbances) over time. This new situation would be perceived in a control room through lower likelihood values in a trend plot in the course of time. The successful applications are in the speech processing field, including speech recognition and speaker verification, since the seventies (Rabiner, 1989). More recently, other fields have experienced its potential, namely telecommunications (Cappe et al., 2010), bioinformatics (Kosky, 2002), and financial engineering (Mamom and Elliott, 2007).

Then, a hidden Markov model-based monitoring system, characteristic of fuel pressure drops higher than 1000 Pa across the second economizer (a critical condition in the present boiler), was constructed. In sequence, lower control limits were calculated for a set of fuel gas pressure drops across it. (The correlation of fuel gas pressure drop measurements across this heat exchanger with those across the convector and the first economizer is close to 1. These heat exchangers are the most critical regarding ash deposits accumulation (Vakkilainen, 2005)). Table 2 summarizes the results. For instance, a model output above –36.1 given by the monitoring system means that it is already possible to have a pressure drop across the second economizer higher than 850 Pa. Figure 4a shows the significant correlation (ρ = 0.985) between the model outputs (likelihood values) and the measurements of fuel gas pressure drops across the second economizer (∆PEcoII). Higher the monitoring system outputs, greater the fuel gas pressure drop (towards to the higher values above 1000 Pa this boiler can undergo in practice). This result illustrates the use of hidden Markov models as decision support systems in monitoring tasks. Figure 4b shows the resulting monitoring chart.

Hidden Markov models are able to handle noisy data, spatial and serial correlations, and non-Gaussian distributions. These features are valuable for developing reliable systems regarding abnormal situation management in continuous chemical processes. Its explicit modeling, based on the probability theory and statistics, also allows both getting insights learned by the model about the process, and in the opposite direction adjusting the model parameters to capture the phenomena more efficiently. Other case study in recovery boiler applying this technique with purpose of monitoring is given in Almeida et al. (2008b).

Fault diagnosis

In on-line process monitoring activities diagnosis task arises after the detection of a fault. The goal is to uncover the root causes in order to intervene and normalize the operations. On one side the pressure for fast decision makings, and on the other hand interactions among process variables and dynamic operations, make it a hard task in practice. Usually fault diagnosis is carried out off-line with the aim of learning and then avoiding the same occurrence in the future.

The following study is given in Almeida et al. (2012). The focus is also a recovery boiler from a pulp mill in Brazil. The collected database refers to four months of operation. It has fifteen process variables with about three thousand measurements for each one. Initially, a fault detection system for monitoring the output steam flow rate was obtained. It was based on a multi-layer perceptron (MLP), which is the most employed artificial neural network model for chemical process description since the nineties (Bulsari, 1995). The monitoring task made use of the Shewhart control chart for individual measurements (Montgomery, 2004). On September 3rd, a fault condition was detected by such monitoring system (Figure 5; register 2204).

Due to the human being capacity for processing visual information, data visualization techniques are the most powerful tools that can help analysts to deal with very large data sets (Marakas, 2002). Here, parallel coordinate plots were used for accomplishing fault diagnosis, with the aim of uncovering the root causes of the event previously classified as faulty. This data visualization technique provides a simultaneous projection of multidimensional data onto a single plane (Inselberg, 2009, 1985). As an example, consider that in a given sample time, the flow rate (F), the temperature (T) and the pressure (P) of the output steam are equal to 297.8 ton/h.
740.2 °C and 6.4 MPa, respectively. Figure 6a shows the representation of this 3-dimensional point (297.8, 740.2, 6.4) in the commonly used orthogonal Euclidean space. This point in such space becomes a polygonal line in the parallel space, as shown in Figure 6b, where each vertical axis (coordinate) represents a process variable. This approach provides an extension of the Euclidean space, since theoretically an unlimited number of variables can be represented. Due to interactions, simultaneous visualization of several process variables is valuable. Now, consider a set of successively collected multivariate data points as is the case regarding recovery boilers. Plotting them in a parallel coordinate plot results in a corresponding set of polygonal lines, each one associated to a specific sample time. The simultaneous visualization of several variables, together with this time information, made the understanding of the interactions among them as well as the dynamic behavior of the boiler easier.

Figure 7 shows the final parallel coordinate plot presented in the study. It was possible to visualize two distinct but normal modes of operation in the boiler during the period encompassing register 2204 (Figure 5). The former, between registers 2192 and 2201 (group of black lines), is characterized by low black liquor flow rates (F-BL) and high dry solids contents (C-DS), whereas the latter, from register 2216 up to register 2224 (group of red lines), had the opposite condition. From register 2202 (green line), register 2203 (blue line), register 2204 (thick red line), until register 2215 starting from register 2205 (group of light green lines), there was in fact a period of transition between both normal modes of operation, rather than a faulty condition as stated by the fault detection system (Figure 5). The stabilization of the boiler could also be visualized. The steam drum pressure (P-SD) returned to the same operating range as before the transition period. Thereafter, there was also the stabilization of the output steam flow rate (F-HPS). (Both occurrences can be noted by means of the overlapping of the groups of black and red lines.) Perceptions like these are valuable in order to achieve more efficient operations.

Figure 8 presents univariate trend plots, which are commonly used in mill control rooms worldwide, for the same operating interval as in Figure 7. The easier way to extract information from parallel coordinate plots in comparison to a simultaneous analysis of a set of trend plots is clear. Such information refer to dynamic behavior, interactions among process variables, modes of operation, and anomalous data. It can also support the setting of more reliable alarm levels (not shown). In brief, visual data analytics in recovery boilers may benefit by the use of multidimensional data visualization tools, as are parallel coordinate plots.
Continuous chemical processes suffer from an inherent variability even under fixed conditions. The problem arises when the operations significantly exceed it. For example, consider a fixed black liquor flow rate of 50 m$^3$/h and dry solids content of 74%. Figure 9a shows the dispersion in the flow rate of the primary combustion air. The corresponding coefficient of variation (coefficient of variation = sample standard deviation / sample mean) is equal to 5.4%. The variability in input process variables cause variations in the outputs. Figure 9b shows the case for the output steam flow rate having a variation around 100 ton/h. The corresponding coefficient of variation is equal to 7.9%. (Such values can be considered satisfactory or not depending on the mill.) More than one operating condition can also be noted in Figure 9a. This short example shows the relevance of the subject. Undesired process variable dispersion is what we are calling abnormal operating variability. The resulting operating inefficiency is responsible for losses mainly economic. Its detection is not an easy task.

The following study (Almeida and Park, 2012a) employed principal component analysis to identify and determine more efficient operating regions regarding steam production. The case study also employs a recovery boiler from a pulp mill in Brazil. The collected database containing eleven process variables refers to one month of operation, with a sample time of five minutes. The goal was to determine combustion air operating regions related to higher steam generation efficiencies (concerning variability reduction), given a fixed dry solids flow (in m$^3$/h).

Principal component analysis is a multivariate statistics technique. Its main purpose is dimensionality reduction contributing to an easier handling and understanding of multivariate systems such as recovery boilers. The key point is its capacity to explain most of the variability present in a data set, composed by p process variables, through only k linear combinations of them, being k << p. Such combinations, called principal components, are the axes of a new coordinate system, derived by rotation of the original one. Their directions are those of maximum variance (Joelíffé, 2002). Most applications of principal component analysis in the chemical engineering field are related to process monitoring since the nineties (Piovoso and Kosanovich, 1996; Kresta et al. 1991). The multivariate control charts usually employ both monitoring metrics Q and T2. Another possibility (illustrated in this study) is its use based on operating regions (windows) (Wang, 1999). This approach is still little explored in chemical industries worldwide.

Initially, a filtered database including only samples associated to black liquor flow rates of 50 m$^3$/h and dry solids contents of 74% was prepared. This combination refers to the most frequent operating condition in the boiler. In sequence, a model based on principal component analysis was obtained. Its first three components were able to explain 80% of the total variance in the original data, composed by eight process variables related to combustion air. Hence, it was possible to describe the system under analysis using a smaller number of dimensions (since k = 3 and p = 8), which makes its handling, visualization, and understanding easier. After a validation step, operating regions related to higher steam production were determined. Figure 10a shows scatter plots for all possible combinations among the three principal components (cp1, cp2 and cp3), where samples related to steam flow rates higher than 270 ton/h are highlighted (blue points). It can be verified that higher steam generation efficiencies are associated to specific regions. Remember that this result is derived from a fixed operating condition in the boiler, given by black liquor flow rates of 50 m$^3$/h and dry solids content of 74%. Figure 10b shows the optimum operating ranges (concerning higher steam production) for the eight original process variables (which were used in the model construction) considering the operating region highlighted in Figure 10a. For instance, the secondary air flow rate (F-SA) should operate above whereas its temperature (T-SA) should remain below the respective mean operating values.

In practice, multivariate control charts using operating regions can be employed to keep the process condition inside desired operating ranges (not shown), which are defined as optimum according to pre-established criteria. This control chart may provide information about the current state as well as the trend of the operations. Concluding, unexpected variations of key process variables are responsible for abnormal process variability. Its identification and diagnosis contribute to more effective actions towards it.

Figure 8. Trend plots for the same operating interval as in Figure 7.

Detection of abnormal operating variability

Figure 9. Operating variability in the a) primary combustion air and b) output steam flow rate, for a fixed black liquor flow rate (50 ton/h) and dry solids content (74%).
Figure 10. a) Optimum operating regions given by steam flow rates higher than 270 ton/h (blue points), where c1p1, c2p2 and c3p3 are the resulting scores of the principal component analysis, and b) operating ranges (blue points) of the combustion air variables associated to the optimum operating region highlighted in a).

its reduction. The result is the achievement of more stable operations and lower maintenance costs.

Management of false alarm rates

An inherent characteristic of continuous chemical processes is the presence of multiple states of normal operation with frequent transitions between them. For instance, black liquor flow rates fed to recovery boilers change from time to time inside a considerable operating range (Figure 11a). Higher number of normal states pose another difficulty regarding the development of reliable monitoring systems: How to manage them in order to achieve reasonable false alarm rates?

This point motivates the study in Almeida and Park (2012b). The data comprehends three months of operation of a recovery boiler from a pulp mill in Brazil, with a five minutes sample time. The operations were considered normal during the whole period. The case study refers to the critical situation concerning thermal efficiency reduction that may happen in the heat section due to ash deposits accumulation. Common practices worldwide are routine patrols around the boiler and monitoring of key process variables, namely those measured after both the super-heater (TSH, in °C) and the boiler bank (TBB, in °C). Under normal conditions, they present a high positive correlation. The goal was to verify the capacity of hidden Markov models (described in a previous section) to manage false alarm rates. Its ergodic topology was adopted. Theoretically, such model structure allows the description of any transition that occurs in practice between the normal states. Figure 11b shows three Gaussian probability distributions each one associated to a particular state of the model constructed. An overlapping of the whole region given by the temperature ranges (TSH and TBB) can be observed with each distribution covering a portion of the data in particular. This specialization means that the model is able to describe specific boilers’ operating conditions (given by distinct black liquor flow rates; shown for 25, 40 and 50 m³/h), as desired.

Table 3 summarizes the quantitative results to false alarm rates. The performance of the hidden Markov model-based monitoring system was compared to monitoring systems based on principal component analysis, a well-established multivariate statistical process control technique (Piovoso and Kosanovich, 1996; Kresta et al., 1991), and on self-organizing maps, a computational intelligence technique (Kollonen, 1995). Both of them were employed in a dynamic way. For a fair basis comparison, they were previously adjusted to give the same false alarm rate as the hidden Markov model-based monitoring system, equal to 4.5% (first row of Table 3). Two independent test data sets were then used. Unlike the former, all data samples in the latter consist of transition periods between normal states in the boiler. To the first, the false alarm rate given by the hidden Markov model-based system was slightly worse than the others (9.1% against 8.8% and 8.1%) (second row of Table 3), whereas to the second (third row of Table 3), the false alarm rate compared to the others was significantly lower (8.3% against 15.1% and 11.6%). This result suggests its potential in handling multiple normal modes of operation, an inherent and challenging characteristic of continuous industrial chemical processes as are recovery boilers, contributing to more satisfactory false alarm rates. Also, the proximity of both rates (9.1% and 8.3%) suggests its ability to deal with normal transitions in a more stable way. The reason for this relates to the specialization of the model in describing the multiple normal modes of operation (Figure 11b).

Hence, the hidden Markov model approach may contribute to reach reasonable false alarm rates once it may handle multiple states of normal operation. This ability is also welcomed to achieve early fault detection since it competes with satisfactory false alarm rates. Both issues are crucial for developing automatic and reliable fault detection systems, yet an open question in practice.

Figure 11. a) Multiple normal operating states, and b) overlapping of the whole operating range, defined by TSH and TBB (temperature normalized values), by Gaussian probability distributions (each one belonging to a particular model state), and association of them with boilers’ operating conditions, given by distinct black liquor flow rates (shown for 25, 40 and 50 m³/h).

Final considerations

From a set of real case studies, examples of utilization of process historical data in recovery boilers were illustrated. Its complex operation, by being multivariate, non linear, noisy and of partial knowledge, as chemical processes usually are, makes hard a pure mathematical description of it. Despite the knowledge accumulated over the years, naturally there are knowledge, insights and perceptions to be still uncovered. This scenario, in conjunction to a plenty of process variables continuously collected through a multitude of plant sensors nowadays, has encouraged the employment of data-driven approaches since the nineties. Current applications involve mainly the use of both techniques principal component analysis and (feedforward) artificial neural networks. This chapter illustrated the use of multivariate statistics, computational intelligence, and signal processing tools. The applications covered sensitivity analysis, visual representations, communication facilities, abnormal situation management, fault detection and diagnosis, visual analytics, abnormal variability detection, handling of multiple normal operating states, and minimization of false alarm rates.

Concluding, the growing availability of very large data sets in chemical industries worldwide in the last years established another paradigm. The poor-data world, where getting data to finish...
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XXL RECOVERY BOILERS - HOW WE DEVELOPED THEM

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Introduction

The chemical wood pulp production has during the last decades grown with about 2-3 Mt/a. This capacity increase consists of new installations, including green field mills and capacity increases on existing recovery boilers. The main part of the new projects is hardwood lines operating on planted eucalyptus and acacia. Those mills are typically located in South America and Far East.

New developments in technology have made it possible to take advantage of the economy of scale when building those new big pulping lines. Obviously the recovery boilers had to grow in size in order to meet the production capacity in the large new single line pulp mills. Excellent process and availability experiences from big and XL size recovery boilers have smoothened the way to XXL size recovery boilers.

The new XXL size recovery boilers are characterised by high black liquor firing capacity, high dry solids content, high power features, low air emissions and environmentally friendly process solutions like burning non condensable gases (NCG) and other side streams coming from other parts of the mill.

High power XXL size recovery boilers are becoming more and more common in pulp mill industry as electricity price has increased. Electricity produced by recovery boilers is seen as green energy in many countries meaning incentives to electricity price which make high power feature investments more profitable.

Other interests are in reductions in usage of fossil fuels and with high power recovery boilers it is possible use less fossil fuels like coal, oil and natural gas in power boilers if located at pulp mill site. This trend means that new technical features used now in recovery boilers have been adapted from power boilers like high steam parameters, high pressure feed water heaters, high combustion air temperatures, flue gas coolers etc. These new solutions have caused certain changes to present designs of recovery boilers compared to units built 10-20 years ago.

World’s biggest boilers consist of the latest design from environmental point of view; all NCG and vent gases are burnt in recovery boiler. Diluted non condensable gas, weak gas (DNCG) dissolving tank and mixing tank vent gases are typically introduced to the high secondary air system, concentrated non condensable gas, strong gas (CNCG) burner is located at secondary air level. Boilers are also designed for high dry solids firing of 80% or higher black liquor dry solids content in virgin black liquor.

The plant designs have been made in PDMS which has given a complete 3D model of recovery boiler including all details. The PDMS model is also of great help in the erection phase. Other sophisticated engineering tools like computational fluid dynamics (CFD), fouling advisor, recovery boiler designer (RBD) have been used when big recovery boilers have been designed.
Very important nowadays when engineering XXL size recovery boilers is the knowledge of corrosion theory because huge boilers have a lot of heating surfaces and it is not possible that those units will encounter sudden corrosion because production losses of big pulp mills would be huge.

**Increase of recovery boiler size during last decades**

Pulp mill and so also recovery boiler capacity has increased a lot during last decades. In the beginning of 1980s there was a common opinion that recovery boilers had reached their maximum physical dimensions. During that time the floor cross section was about 100-120 m². However, one recovery boiler in Finland started up in 1990 which had black liquor firing capacity of 2600 tds/d. Boiler can be called as first so called XL size recovery boiler. This big boiler was some kind of threshold for other coming big boilers. This boiler was also a forerunner for black liquor high dry solids firing, CNCG combustion and bio sludge combustion. Six years later the first 3800 tds/d boiler was started up in Indonesia. At that mill there are three similar boilers which have been upgraded to the load of 4000 tds/d. Boiler can be called as first so called XL size recovery boiler. This big boiler was some kind of threshold for other coming big boilers. This boiler was also a forerunner for black liquor high dry solids firing, CNCG combustion and bio sludge combustion. Six years later the first 3800 tds/d boiler was started up in Indonesia. At that mill there are three similar boilers which have been upgraded to the load of 4000 tds/d. Development continued. Again after eight years first so called XXL size 5500 tds/d recovery boiler was delivered to China. With that boiler 6000 tds/d peak load was reached in 2005 and it was world record during that time. Figures 1 and 2 show how the size of recovery boilers has increased during last decades. The pictures also shown the floor area and start-up year of those boilers.

Two 7000 tds/d boilers started up in 2010 in Indonesia and in China. Those boilers have floor area of 293 m² and furnace total height is 64.5 m. Boilers have quite traditional steam parameters; temperature is 480 °C and pressure 84 bar and their gross steam generation is 285 kg/s. They do not have any high power features except 80% black liquor dry solids content. Mainly they are burning Eucalyptus and Acacia black liquors.

Boilers are sister boilers except that the boiler in China has Quaternary air level for reducing NOx emissions. This also means that composite tube level on furnace walls is extending higher than in Indonesia boiler.

Present biggest recovery boiler in the world is located in Brazil and its floor area is 323 m² and furnace total height is 68.2 m. Its main steam temperature is 492 °C and pressure 94 bar. Steam is generated 325 kg/s and boiler has certain high power features like high dry solids firing (80%), all combustion airs are heated to 185 °C, feed water tank is so called full pressure tank (140 °C), feed water before economizer 1 is heated to 160 °C in preheater. As can be noticed the boiler does not have very high steam parameters and that has been typical for big boilers. Boiler was started up successfully in January 2014.

What will happen in the future? Even bigger and bigger boilers have been discussed and most probably 10000 tds/d load will be exceeded in a couple of years, Figure 2.

Most interesting from above values is furnace height. As can be seen it is only about two times taller in big unit than in small one. Other parameters are varying much more between those two compared boilers and differences are more logical to understand. Some design criteria in recovery boilers are furnace volume load and flue gas residence time in the furnace. In small boilers volume load can be 160 MW/m³ and corresponding value in big boilers has typically been 80-100 MW/m³. Volume load is indicating also what flue gas residence time in the furnace is and in small boilers it is 3.5-4.5 s and in big units 7-8 s (calculated from floor to nose). Theoretically the furnace of big recovery

Figure 1. Capacity increase of recovery boilers.

Figure 2. Boiler sizes higher than 5500 tds/d.

Figure 3 shows what are certain physical differences between small and big recovery boilers. On the left hand side of the figure there is shown one new small boiler delivered to India in 2013. This boiler size was quite typical about 30-40 years ago. The middle one is built in the beginning of 1990 and the boiler on the right is world’s biggest recovery boiler. If we compare certain design parameters between smallest and biggest ones we can see the following differences:

- Capacity is 11.7 times higher
- Floor area is 7.9 times bigger
- Furnace total height is 2.1 times taller
- Furnace volume is 16.9 time bigger

Most interesting from above values is furnace height. As can be seen it is only about two times taller in big unit than in small one. Other parameters are varying much more between those two compared boilers and differences are more logical to understand. Some design criteria in recovery boilers are furnace volume load and flue gas residence time in the furnace. In small boilers volume load can be 160 MW/m³ and corresponding value in big boilers has typically been 80-100 MW/m³. Volume load is indicating also what flue gas residence time in the furnace is and in small boilers it is 3.5-4.5 s and in big units 7-8 s (calculated from floor to nose). Theoretically the furnace of big recovery

Figure 3. Comparison of boilers’ physical sizes in real scale.
boiler is not needed to be as tall as it is if only volume load and residence time had taken into account because many small boilers are operated well with above mentioned design parameters. However, when furnace height is determined then also flue gas temperature after furnace and superheaters, sticky area location etc. must be considered.

Figure 4 shows world’s biggest recovery boiler height vs. hotel Ilves which is a famous hotel in Tampere. As can be seen the recovery boiler located in Brazil is about 23 m taller than hotel Ilves.

Figure 5 shows how recovery boilers’ black liquor burning capacity has increased since 1970 based on our reference list. As can be seen about in 1990 black liquor burning capacity exceeds 2000 tds/d load. Real big step happened in 2004 when boiler load increased from 3800 tds/d to 5500 tds/d.

One of the most important design criteria in recovery boilers is a floor loading. Floor loading is calculated by using black liquor dry solids higher heating value (HHV), black liquor load and furnace floor area. Nowadays typical floor load design in big boilers is about 3.5 MW/m² or even higher when it was earlier 2.0-3.0 MW/m². In some new upgrade cases even 3.8-4.0 MW/m² floor loads have been operated.

Why is it possible to have so high floor loading? Nowadays black liquor dry solids content starts to be 80 % (earlier it was 60-70%), boilers have modern control systems, air systems and black liquor firing practices have been developed a lot during last decades, etc. Figure 6 shows how floor loadings have developed during the last 35 years. Blue dots are indicating floor loading with unit of tds/d/m² and red ones are for MW/m². As can be seen somewhere in the middle of 1990’s floor loading exceeded 3.0 MW/m². As an example from the floor loadings we could analyze world’s biggest recovery boiler; if it had dimensioned by using 2.5 MW/m² loading then floor area would be 452 m² instead of 323 m². This would mean 21 m furnace width and depth compared to the design of 18.3 m x 17.7 m furnace.

Figure 7 shows how floor area has been increased during the last decades. From mid 1970s to mid 1980s in eight years period the floor area increased by 45% and then in the following 8 years by 26%. From 1992 to 2004 floor cross section increased only by 3% meaning about 0.25% annually. Then suddenly the area jumped upward by 43% when big recovery boiler in China started up. After this project the furnace size has increased quite steadily meaning about 20% in ten years. As can be noticed from the Figure 7 the highest floor area increase and also boiler load increase happened in 2004. Before and after that average boiler floor area has increased by 3% and 1.3% annually.

Pre-engineering of first XXL size recovery boiler

In the beginning of 2000 special development project was carried out in order to study possibilities to build and deliver a real big recovery boiler. Main emphasize in that project was to identify possible items/designs which may affect boiler availability, furnace processes and mechanical design. All boiler parts and equipment were analyzed and when certain risk item was detected then it received a code number for further analysis, see Figure 8.
Every item was studied deeper by using for example risk analysis. When certain risks were detected then action plans were developed in order to find corrective actions. As an example code 19 which is located just beside secondary superheater. When this item was analyzed then main targets were concentrating on manufacturing of very long elements (22-25 m), how forth and back movement of elements is minimized especially during boiler start ups when heating surfaces are relatively clean but sootblowers are used etc. in economizer and boiler bank areas long 24-27 m elements are very flexible and therefore it was important to find solution for minimizing sideward vibration/movement of elements.

After this study we principally had a readymade big recovery boiler concept for upcoming big pulp mills. Soon after this work first inquiry of XXL size recovery boiler came and it was very easy to start to prepare technical specification when knowing how this kind of big unit should be built. That project was awarded to us in 2002. Some physical facts from XXL size recovery boilers

Steam boilers are built by using a lot of tubes, pipes, downcomers, headers etc. Table 1 shows how much heating surface tubes are there in world’s biggest recovery boiler. As can be seen total amount of tubes is about 500 km. Distance from Tampere to Helsinki is 170 km and so this boiler has three times more tubes than this distance. There are still many other pipes in recovery boilers which are not listed in the table like downcomers, headers, main steam pipe, drain and vent pipes, process pipes etc. If those are added then total tube/pipe length is close to 600 km.

Table 1. Heating surface tubes in world’s biggest recovery boiler.

<table>
<thead>
<tr>
<th>Heating surface</th>
<th>Tube amount (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Economizers</td>
<td>192</td>
</tr>
<tr>
<td>Boiler Bank</td>
<td>55</td>
</tr>
<tr>
<td>Screen tubes</td>
<td>43</td>
</tr>
<tr>
<td>Primary I SH</td>
<td>22</td>
</tr>
<tr>
<td>Primary II SH</td>
<td>22</td>
</tr>
<tr>
<td>Secondary SH</td>
<td>29</td>
</tr>
<tr>
<td>Tertiary SH</td>
<td>29</td>
</tr>
<tr>
<td>Quaternary SH</td>
<td>25</td>
</tr>
<tr>
<td>SH Total</td>
<td>149</td>
</tr>
<tr>
<td>Furnace walls</td>
<td>83</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td>~ 500</td>
</tr>
</tbody>
</table>

As an example in world’s biggest recovery boiler there is about 190 m furnace downcomer pipes with size of 711 x 55 mm (Outer diameter OD x wall thickness). Weight of this pipe is 890 kg/m and so total weight of downcomers is about 170 tons.

Furnace lower part is made by using composite material (AISI 304L or Sanicro 38) which consists of carbon steel base material and outer layer of stain less steel material. In above mentioned boiler there is about 18 km this composite material. Material grades of those heating surfaces mentioned in Table 1 are typically the following (EN and ASME materials) Table 2.

Figure 9 shows tubes/elements for manufacturing of boiler bank in one big recovery boiler. On the left hand side there are bundles of tubes which have come from the tube supplier and on the right hand side there is the output from the manufacturing process; a readymade boiler bank package for transportation.

Heaviest single component in recovery boiler is a steam drum. It is principally heart of a recovery boiler. Purpose of the steam drum is to separate water and steam from each others. In Figure 10a shows the steam drum of one big boiler on the truck when transporting it from the manufacturing facility to harbor for sea transportation. In Figure 10b there is erection of steam drum going on in one XXL size boiler in China. Figure 10c shows drum inside of world’s biggest recovery boiler ready for installation of steam drum internals. In Figure 10d there is welding of risers going on.

In big recovery boilers the weight of steam drum can be 150-200 tons, its length can be about 20 m, outer diameter 2.4 m and wall thickness 120-150 mm.

Table 2. Typical tube materials in recovery boilers.

<table>
<thead>
<tr>
<th>EN</th>
<th>ASME</th>
<th>COMPONENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>P265GH</td>
<td>SA-210 A1</td>
<td>Furnace, primary superheaters, screen tubes, boiler bank, economizers</td>
</tr>
<tr>
<td>16Mo3</td>
<td>SA-209 T1</td>
<td>Furnace, primary superheaters</td>
</tr>
<tr>
<td>Composite 304L</td>
<td>Composite 304L</td>
<td>Lower part of furnace</td>
</tr>
<tr>
<td>13CrMo4-5</td>
<td>SA-213 T11 / T12</td>
<td>Secondary superheaters</td>
</tr>
<tr>
<td>10CrMo9-10</td>
<td>SA-213 T22</td>
<td>Secondary, tertiary and quaternary superheaters</td>
</tr>
<tr>
<td>7CrMoVTiB10-10</td>
<td>SA-213 T24</td>
<td>Tertiary and quaternary superheaters</td>
</tr>
<tr>
<td>X10CrMoVNb9-1</td>
<td>SA-213 T91</td>
<td>Tertiary and quaternary superheaters</td>
</tr>
<tr>
<td>X7CrNiNb18-10 (.4912)</td>
<td>SA-213 TP347H</td>
<td>Hottest superheaters in corrosive atmosphere</td>
</tr>
<tr>
<td>Composite Sanicro 28 and 310, Overlay welded materials</td>
<td>Sanicro 28, overlay welded materials</td>
<td>Hottest superheaters in corrosive atmosphere</td>
</tr>
</tbody>
</table>

Figure 9. Boiler bank tubes and readymade boiler bank elements/package.
Recovery boiler as a multi-fuel boiler

Modern XXL size recovery boilers are multi-fuel boilers. Boilers have latest advanced designs from environmental point of view; all NGC and vent gases are burnt in recovery boiler. DNCG, dissolving tank and mixing tank vent gases are typically introduced to the high secondary air system and so mixed with air. CNCG burner is located at secondary air level.

Figure 11 shows normal fuels burnt in recovery boilers.

Main fuel is of course black liquor coming from the pulping process. Nowadays, very typically as fired dry solids content of black liquor is 80-83%. Black liquor systems are therefore pressurized systems meaning that for example black liquor burning temperature is controlled in heavy black liquor tank to targeted value which can be at the level of 140 °C. Oil and natural gas are typically used during boiler start-ups and shutting down procedures in start-up burners and load burners. In some cases load burners are used for generating more steam to steam net and controlling its pressure. In some softwood mills also soap is burnt by mixing it with black liquor.

Secondary bio-sludge from waste water effluent plant can be mixed with black liquor and burnt in the recovery boiler furnace.

Variety of fuels is causing challenges for boiler optimum design from emissions, corrosion and fouling point of view. Therefore when boilers are designed it is very important to know all incinerated fuels in order to select furnace size and materials properly. Especially minimizing NOx emissions in XXL size boilers is sometimes causing challenges because many of those fuels are including ammonia which can then generate more NOx emissions.

Table 3 shows an example which fuels are burnt in certain big recovery boilers.

As can be noticed one big boiler in Finland has designed for burning really many fuels. Boiler has been operated now for five years without any problems due to type of fuels.

Materials in XXL size recovery boilers

Furnace floor and walls

XXL size recovery boilers have principally same materials as other recovery boilers have. Furnace lower part has been made by using composite material of AISI 304L/SA-210 A1. This material has been used already nearly for 40 years. Reason for using stainless steel material is a corrosion risk in reducing atmosphere in lower part of furnace. If material would be carbon steel and we have a high pressure boiler which has tube surface temperature 320-330 °C then tube corrosion is very evident in environment which exists in furnace lower part.

Floor tubes are typically made by carbon steel and that is possible because they are protected during operation by frozen smelt layer. Earlier it was common to make floor also by composite tube (AISI 304L) but in some boilers stainless steel outer layer cracking has been encountered. When cracks exist there is always risk that they penetrate trough carbon steel base material and therefore water leak may occur and worst scenario is smelt water explosion. Reasons for cracking are not 100% sure but they are initiated...
due to tensile stresses prevailing in stainless steel layer when tube surface temperature has been high and stainless steel part has yielded, Figure 11.

Due to cracking problems in 304 L composite tubes new materials have been developed for replacing that material on floors and in some other critical areas in recovery boiler lower furnace like in primary air port openings. One developed material is Sanicro 38 composite tube. In this material outer layer has about 40% Ni and 20% Cr whereas in 304L material Ni is 10% and Cr 20%. Also heat expansion coefficient of Sanicro 38 outer layer is closer to carbon steel than in 304L which is beneficial from thermal stresses point of view. Figure 12 shows main material alternatives in recovery boiler furnace.

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Figure 11. Composite floor and cracks in tubes and membranes.

Figure 12. Tube material alternatives in recovery boiler furnace.

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Figure 13 shows modern material selection in XXL size recovery boiler floor area. As can be seen the floor heart is made by carbon steel material. Floor bends toward front and rear walls, side most tubes adjacent to side walls and primary air port bended tubes are made by Sanicro 38 material. This kind of design has proven to be a very reliable solution.

Figure 13. Material selection of floor and lower part of furnace.

On Figure 14 there is a lower part of furnace during erection of one XXL size recovery boiler.

Figure 14. Furnace lower part during erection stage.

Superheaters
One of the most challenging material selections in recovery boiler is superheaters. Typically in recovery boilers many kind of corrosion phenomena can be detected in heating surfaces as is shown in Figure 15. Many of those corrosion have been managed to minimize in modern recovery boilers:

• Acidic sulfates are not formed any more as easily as earlier due to high dry solids firing, good air systems, low sulfidity level in eucalyptus and acacia mills.

Figure 15. Occurrence of corrosion in recovery boilers.

• High dry solids firing and good air systems with effective air/flue gas mixing have minimized risks to sulfidation corrosion in furnace.

• Optimized material selection with increased knowledge of K (potassium) and Cl (Chlorine) chemistry and their effect to superheater corrosion have decreased corrosion findings in superheater areas.

In new recovery boilers there is a clear trend to have higher steam parameters in order to increase electricity production. This has caused special challenges to superheater material selection and how to prevent sudden corrosion. In XXL size recovery boilers there can be 150 km superheater tube materials and everybody can imagine that what could happen if tubes are corroded and boiler will have unplanned stop due to heavy material losses. Big mills can produce pulp 1.5 million ADt/a meaning about 4200 ADt per day. If pulp price is US$ 1000 per ton then losses of income can be US$ 4.2 million per day. Very typically when superheaters are repaired due to unpredicted failures then outage may take at least 4–7 days from liquor to liquor depending of course on how severe damages are. Figure 16 shows secondary and tertiary superheaters hanging from the furnace roof when one XXL size recovery boiler is in under erection. Length of elements is about 24 meters.
Molten phase corrosion may be very severe in hottest superheater stages. It occurs when ash/deposit melts on the tube surface. This corrosion is controlled by the first melting temperature (FMT) of the deposit. The FMT is the temperature, at which the first melt appears in the deposit (also known as T0). Main contributors to FMT are chlorine (Cl) and potassium (K). High amount of carbonates (CO3) i.e. carryover lowers also the FMT of the deposits. Even small amount of sulfides (0.1 wt-%) in the deposits lowers the FMT about 50 °C.

The most challenging superheater stages are hottest ones from where superheated steam is going to main steam net. Figure 17 shows an example from the corroded tubes in the hottest superheater stage.

Table 4 shows a couple of recovery boiler references with stainless steel materials in superheaters.

<table>
<thead>
<tr>
<th>Project</th>
<th>SH steam outlet temperature (°C)</th>
<th>Stainless steel material in hottest stages</th>
<th>Ash handling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiler A</td>
<td>505</td>
<td>8/T</td>
<td>Yes</td>
</tr>
<tr>
<td>Boiler B</td>
<td>480</td>
<td>N/A</td>
<td>Yes</td>
</tr>
<tr>
<td>Boiler C</td>
<td>480</td>
<td>4/S and 4/T</td>
<td>Yes</td>
</tr>
<tr>
<td>Boiler D</td>
<td>485</td>
<td>1/T</td>
<td>Yes</td>
</tr>
<tr>
<td>Boiler E</td>
<td>487</td>
<td>2/T</td>
<td>Yes</td>
</tr>
<tr>
<td>Boiler F</td>
<td>460</td>
<td>1/S and 4/T</td>
<td>Yes</td>
</tr>
<tr>
<td>Boiler G</td>
<td>487</td>
<td>1T asin 4/Q</td>
<td>Yes</td>
</tr>
<tr>
<td>Boiler H</td>
<td>492</td>
<td>1/T</td>
<td>Yes</td>
</tr>
</tbody>
</table>

XXL size recovery boilers have been operated extremely well from process and mechanical point of view. Flue gas emissions like SO2 and TRS have been typically at the level of zero. NOx emission targets have been managed to reach with normal air systems and when lower values are required then more air staging has been used by installing Quaternary air level. Figure 18 shows a couple of examples from one XXL size boiler operation. In Figure 18a there is black liquor load and steam generation when capacity test was carried out. Virgin black liquor load was about 7200 tds/d and corresponding fired load was 7700 tds/d. Steam generation during test was targeted to be 300 kg/s. In Figure 18b there are reduction rate values when boiler had a performance test. Measured values in smelt exceeded 97% which is really good result. Reduction rate is one of the most important performance data which is followed during boiler operation. It tells how much sulphate (Na2SO4) is reduced to sodium sulphide (Na2S) in charcoal bed. Figure 18c indicates what has been oxygen level in flue gases after economizers. Low value means good combustion process in the furnace and it also indicates low flue gas heat losses.
Summary

New green field pulp mills are huge. Pulp production starts to be 1.5-2.0 million ADt/a. This means that also the size of recovery boilers has come very big. Boiler size for those big mills is about 7000-8000 tds/d. Valmet has delivered many boilers which have had a capacity of 4000-5000 tds/d and experiences from those references have been extremely important when developing even bigger boilers like XXL size units. We have also seen certain difficulties in those boilers but all problems have been successfully solved and therefore we have been very confident with our design when bigger and bigger boilers are built.

XXL size recovery boilers have operated really well and availability has been good. From process point of view we have not experienced any setbacks. Mechanically certain big components have caused challenges mainly due to unexpected movement of elements but they have been managed to fix in normal outages meaning that no abnormal availability problems have been encountered.

Bigger and bigger boilers are planned to build and therefore we feel very confident for those coming Magnum size boilers because the references which are working well are a must in order to get customers trust on your technology and on you as a reliable supplier.
HIGH ENERGY RECOVERY BOILERS

MARJA HEINOLA AND KEIJO SALMENOJA
ANDRITZ OY
FINLAND

Introduction

The kraft recovery boiler is always referred as the heart of the pulp mill and is the critical component in the closed loop producing energy alongside recovering the cooking chemicals. As long as the heart sustains well, other systems excel. Today the mills, constrained with rising energy cost and security of supply strive to maximize green energy to substitute fossil fuel and attain self-sufficiency.

Modern non-integrated pulp mills are nowadays totally self-sufficient in respect to steam and power production, and the idea of producing and selling not only pulp, but also electricity is already a reality at many mills. Even though a mill is self-sufficient in energy, there are normally still many areas where energy could be saved and electricity production could be increased. The market is globally demanding less pollution per produced megawatts (MW) and better utilization of renewable resources.

The change to increase power production from kraft recovery boilers has been quite rapid. In the 1990s, when new mill or new recovery boiler was supplied, energy efficiency was not a topic. Today almost in all new cases, however, energy efficiency is the topic number one. Figure 1 shows the development of power production from recovery boilers equipped with high-energy features and the possibilities to increase energy efficiency at kraft pulp mills. To be able to increase the energy efficiency of the pulp mills, efforts to decrease the consumption of energy at the mills has to be on the focus, too.

Since the focus has earlier been on the chemical recovery and not on the power production, the power generation efficiency (power-to-heat-ratio) has always been rather low in traditional boilers. In order to improve the power generation from the recovery boilers, several technical solutions have been developed and adopted. It is not, however, only in the recovery boiler area where savings can be done, but it is possible to achieve significant savings also in other process areas.

Power production in modern mills is presently around 1100 kWh/ADt at a softwood mill and around 900 kWh/ADt at a hardwood mill. Power consumption at softwood and hardwood mills is ca. 600 kWh/ADt and 500 kWh/ADt, respectively (Figure 2) (Salmenoja & Heinola 2013).
Due to the originally poor power generation efficiency, several improving features have been applied to the recovery boiler. The high-energy recovery boiler (HERB) concept was developed for this purpose. It increases the power generation efficiency further than what is possible with traditional increase of the steam parameters. The HERB concept was the answer to the demand to increase the power-to-heat-ratio and power production of recovery boilers. The first HERB with a steam temperature of 505 °C was started up in 2004 in Finland. Figure 4 shows the side view of the 2004 vintage first HERB.

The main factor limiting the increase of power production from recovery boilers is corrosion. Therefore, the development in the steam outlet temperature in kraft recovery boilers has been extremely slow compared to power boilers. Japanese boiler manufacturers have been the pioneers with high-temperature recovery boilers. The first recovery boiler having a steam outlet temperature of 500 °C was started up in Japan in 1983. Recovery boiler with steam outlet temperature of 515 °C was started also in Japan in 1988 (Arakawa et al. 2005). The highest steam outlet temperature utilized in kraft recovery boilers is still 515 °C.

Recovery boilers having higher steam outlet temperature than 515 °C are not in operation. Figure 3 shows the development of steam parameters in kraft recovery boilers from 1930s (Vakkilainen, 2005).

With a modern high-energy recovery boiler, mills can easily double their power production compared to an old recovery boiler. There are several ways to increase the power production from a recovery boiler and some of those may also include operational risks.

This paper recapitulates measures to increase power production from recovery boilers and summarizes practical experiences from operating high-energy recovery boilers.

**High-energy recovery boiler concept**

Power generation, in combined heat and power system (CHP) is described in terms of the power generation efficiency (PGE) or the power-to-heat-ratio. In order to improve the power generation, high-energy recovery boilers employ several technical solutions.

There are several ways to increase the power production from a kraft recovery boiler and totally, some 20 MW more power can be produced by different measures. However, some of the measures may include operational risks, which should be taken into account. The following is not a comprehensive list, but shows the most commonly used measures to increase power production:

- High dry solids in black liquor
- High steam temperature and pressure
- Sootblowing steam from the turbine
- Preheating of feedwater
- Preheating of combustion air
- Fluegas cooling
- Hot condensate return
- Heat recovery from vent gases
- Interheater
- Reheater

The optimum way to increase the power generation efficiency is to utilize all the methods mentioned above. Although, every measure to increase power production has a price tag, the payback time of most of the measures is very short. Figure 6 shows estimated annual profits available with different options.

**High dry solids**

Dry solid content of black liquor has a large impact on steam generation. It is more effective to evaporate the moisture in a multiple effect evaporator with process heat rather than doing the same inside the furnace. The increase in net steam generation for 65% solids as against 85% solids is approximately 7-8%. Further, with high concentration liquor, it is possible to operate with low excess air, which again minimizes loss to the flue gas. A comparison of heat balance at different dry solid content is furnished in Figure 7.
Steam temperature and pressure

Another methodology for improved PGE is to use higher steam values (McKeough and Savilajru, 2007). Figure 8 shows the power generating efficiency as the function of steam outlet temperature (Rahman and Lehtinen, 2013). However, high-temperature corrosion of superheaters is the main limiting factor of increasing the steam outlet temperature. In general, potassium (K) sets practical constraints in strive towards higher final steam temperatures. Potassium is the main contributor in molten phase corrosion by dictating the first melting temperature (FMT) of the deposits. A rule of thumb has been to keep the material temperatures below the FMT. If molten phases are present on superheater tubes, corrosion rates will be quite high and unpredictable.

With regard to material selection, chloride level in black liquor dictates the need for expensive materials. Chlorine-induced corrosion below the FMT can be handled with material technology, but it necessitates solid knowhow of deposit properties and local material temperatures. Maybe due to this fact, no one has had the courage to exceed 515 °C as the steam outlet temperature in black liquor recovery boilers. The benefit of extremely high steam parameters may diminish due to exorbitant cost of materials.

Sooblowing steam

In older recovery boilers, fresh superheated steam was used to sootblowing. Depending on the boiler and black liquor properties, sootblowing steam consumption can vary from 3% up to 10%. By changing the source from superheated steam to extraction steam from turbine, improvements to the power generation efficiency can be achieved.

Sootblowing steam is typically taken directly from the final superheater steam outlet and is passed through a poppet valve to reduce the pressure from 17 to 24 bar before entering the sootblower feed tube.

Since sootblowers consume 3 to 12% of the total superheated steam produced by the boiler, sootblowing with high pressure steam can be a costly operation. If sootblowers can operate at a lower pressure, for instance, 9 to 14 bar(g), there will be a significant economic advantage to pulp mills. This is because low pressure steam is less valuable than high pressure steam, as it can be taken from the steam turbine exit after the steam has been used to generate electricity.

Feedwater pre-heating

In a high pressure boiler there is usually a large margin between the feedwater temperature to the drum and the drum saturation temperature. In this case the steam generation can be increased by pre-heating the feedwater. First the feedwater can be heated with low pressure steam in the feedwater tank to the maximum temperature. For instance from traditional 120 °C up to 145 °C with low pressure steam. Between the feedwater tank and the economizers the feedwater can be pre-heated with medium pressure steam to 160 °C. Between economizer I and II the feedwater can additionally be heated by 15-20 °C with high pressure extraction steam.

Pre-heating of combustion air

Pre-heating of all combustion air to 190 °C with different level of extraction steam is also a quite cost effective way to produce more steam and hence improve the power generation efficiency. Traditionally, primary and secondary airs are heated up to 120-150 °C. By adding a few air pre-heaters the power production can be increased further.

Fluegas cooling

The above mentioned measures improve the power generation efficiency of the boiler, but the total efficiency of the boiler is slightly lowered due to the higher flue gas temperature. In order to improve the overall efficiency, fluegas cooling after the precipitator could be introduced. If the mill has a deficit of low pressure steam or hot water, or is using a condensing turbine, the fluegas cooling should be exploited.

When cooling the flue gases with 100 °C water (water heated to approx. 150-160 °C) it is possible to set the flue gas temperature in the stack to around 140 °C. The heat from the fluegases can be used for feedwater pre-heating, air pre-heating, hot water production etc.

Summary of the measures

The means are almost unlimited, but the most optimal way to enhance the efficiency of a pulp mill is always a matter of thorough studying of the individual mill’s and department’s balances. The additional production with the solutions mentioned above for a recovery boiler operating at 92 bar(a) and 490 °C with a condensing turbine is presented in Table 1.

<table>
<thead>
<tr>
<th>Features</th>
<th>Net electricity produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedwater pre-heating and interheating</td>
<td>+2.7 MW</td>
</tr>
<tr>
<td>Air pre-heating</td>
<td>+1.0 MW</td>
</tr>
<tr>
<td>Internal sootblowing</td>
<td>+0.6 MW</td>
</tr>
<tr>
<td>Hot primary condensate return</td>
<td>+0.6 MW</td>
</tr>
<tr>
<td>Higher dry solids in BL</td>
<td>+2.0 MW</td>
</tr>
<tr>
<td>Fluegas cooling</td>
<td>+4.5 MW</td>
</tr>
<tr>
<td>Total</td>
<td>+11.4 MW</td>
</tr>
</tbody>
</table>

Practical operating experiences

The first HERB was started up in 2004 in Finland and presently 10 such recovery boilers are in operation. Two boilers are under construction. The first units were not equipped with all the power production enhancing features, but due to encouraging experiences from operating units, new features to further enhance the power production have been adapted.

The first HERB had a relatively high capacity (505 °C, 102 bar). This boiler is still the largest recovery boiler in Finland. The first HERB with a steam outlet temperature of 515 °C was started up in Sweden in 2006. The second HERB with the same steam temperature was started six years later, also in Sweden. Totally, six of the HERBs have steam outlet temperature higher than 500 °C, as shown in Table 2.
When the first unit with the 515 °C steam outlet temperature was started up, steam temperature was gradually increased to the target value, as shown in Figure 10. This was mainly done since previous experiences on high steam outlet temperatures were not available.

After the first scheduled annual shutdown, the boiler was thoroughly inspected. Since no marks of enhanced corrosion or other material degradation was not found, steam temperature was raised permanently to the design value of 515 °C. Since then, the boiler has been running at full load and at designed steam parameters.

Corrosion management
The main reason for excellent experiences from HERBs with high steam outlet temperatures is the low K and Cl content in as-fired black liquor. Proper control of both K and Cl is vitally important to avoid high-temperature corrosion of the hottest superheaters. Since K is the main contributor to the FMT, the only way to avoid molten phase corrosion of superheaters is proper control of K level in as-fired black liquor. High-temperature corrosion cannot be totally avoided although material temperatures are kept below the FMT, since active oxidation is responsible for chlorine-induced corrosion below the FMT. However, active oxidation can be limited by correct material selection (Salmenoja 2000).

At high steam outlet temperatures, special materials must be used in superheaters. The amount of high-alloyed materials is mainly dictated by the Cl content in black liquor and applied steam temperature. In some cases the amount of expensive materials may become extremely large, without proper optimization of the superheater design. To be able to construct cost-effective HERB solutions, a superheater material temperature calculation tool has been developed. It renders it possible to optimize superheater design and the amount of corrosion resistant high-alloyed materials (Figure 11). With this tool it is possible to minimize the amount of expensive materials in superheaters and to assure a long service time with a high availability. The HERB has the same design constraints as the conventional recovery boilers and high steam parameters must not jeopardize pulp mill’s availability.

![Figure 10. Steam outlet temperature during the first operating years in the HERB with steam parameters of 515 °C and 106 bar (Salmenoja and Heinola 2013).](image)

![Figure 11. Example of the outcome from the optimization tool to calculate superheater metal temperatures and to optimize the need for high-alloyed steels.](image)

![Figure 12. A practical example of the effect of material grade on superheater corrosion.](image)

![Figure 13. Measured corrosion rates of several superheater material candidates (Finnish Recovery Boiler Committee 2013).](image)

Increasing the steam outlet temperature also increases applied steam pressure. This in turn means rising furnace wall material temperatures and presently used wall materials may not be used in the future. In the SKYREC project existing and potential new furnace wall materials were field tested with a special test rig. Figures 14 and 15 show the main results of these tests.

FIGURE 10. Steam outlet temperature during the first operating years in the HERB with steam parameters of 515 °C and 106 bar (Salmenoja and Heinola 2013).

FIGURE 11. Example of the outcome from the optimization tool to calculate superheater metal temperatures and to optimize the need for high-alloyed steels.

Figure 12 shows a practical example of the effect of material grades on corrosion rate. It shows a superheater tube sample taken from a recovery boiler suffering from rapid degradation of the hottest tubes. The tube material below the butt weld is austenitic stainless steel and the material above is low-alloyed steel. The reason for rapid material degradation of low-alloyed steel was confirmed to be active oxidation due to high Cl level in as-fired black liquor. As can be seen from the figure, active oxidation can be effectively avoided by using highly alloyed materials, such as austenitic stainless steels.

The HERB has the same design constraints as the conventional recovery boilers and high steam parameters must not jeopardize the pulp mill’s availability. To be able to design a high-energy recovery boiler with a high availability, there are two major things that must be known: 1) material temperatures in superheaters and 2) K and Cl levels in as-fired black liquor. By knowing these two factors, superheater materials can be optimized and their lifetime reliably predicted. The main factor limiting the increase of power production from recovery boilers is corrosion. Therefore, increasing steam outlet temperature and pressure requires a sound knowledge of recovery boiler fluegas chemistry, fly ash behavior, and the control of heat transfer surface temperatures.

Future development challenges
Increased interest in pulp mills to increase the energy efficiency sets increasing requirements for the boiler suppliers to search for new ways to maximize power production from the recovery boiler. This has led us to the basic questions, i.e. what are the practical constraints to maximize the power output. However, every measure that increases power output has also a price tag and they all increase the investment costs. Therefore, a feasibility study should always be made to optimize the configuration to maximize power output.

The SKYREC project aimed at with possible new measures to further increase the power output from kraft recovery boilers (Finnish Recovery Boiler Committee 2013). One objective was to evaluate constraints to aim at even higher steam parameters than the existing 515 °C and 110 bar. The target was set on steam temperature of 540 °C and steam pressure of 160 bar. Several field probe tests were carried out to study the suitability of commonly used materials and new potential materials for superheaters and furnace walls (Figure 13). According to the studies, it seems possible to find feasible materials also for recovery boiler environments at increased temperature and pressure (Finnish Recovery Boiler Committee 2013).
Recovery boiler capacities have been increasing extremely rapidly during the last few years and it seems that this is the trend also in future. This is due to increased pulp mill capacities. New mills are in the 1.5 million ADt/a capacity range, which means that the recovery boiler capacity is around 7000-8000 tds/d. The world’s largest kraft recovery boiler is now under construction (Figure 16). Its capacity is 11600 tds/d and it will be started up in 2016. It will also be the most energy efficient kraft recovery boiler ever built, with steam parameters of 515 °C and 110 bar. It has all the features to maximize the power output.

Further increase in the steam outlet temperature requires larger amounts of more expensive superheater materials. In addition, largely used lower furnace material 3R12 (304L) may not be any more feasible at higher operating pressures. Therefore, new materials need to be searched and tested. The question still remains: could the steam outlet temperature of 540 °C be possible in the future?

Increasing power output brings more power boiler features also to kraft recovery boilers. One practical example is cooling of fluegases after the precipitator. This increases the energy efficiency and power output significantly. Today, fluegases temperatures after the coolers are around 140 °C. But how low can we go with the fluegas temperature without losing the boiler availability?

Emission limits will be tightened in the future. New European legislation sets new and more stringent emissions limits for the recovery boilers. Other countries are following the European route towards lower emissions from kraft recovery boilers. This trend is not a problem with other emissions, except with nitrogen oxide (NOx).

Aiming at high power output with low NOx emissions is somewhat contradictory. Maximizing power output requires high furnace temperatures, but minimizing NOx emissions requires as low temperatures as possible. Therefore, the outcome is always a compromise in this respect.

Summary

There are several ways to increase the power production from a kraft recovery boiler. Totally, slightly over 20 MW more power can be produced by different measures. With the HERB concept, mills can easily double their power production compared to an old recovery boiler. Proper superheater design and optimal heat transfer rate are the key to predicted performance and high steam production. Increasing steam outlet temperature and pressure requires a sound knowledge of recovery boiler fluegas chemistry, fly ash behavior, and the control of heat transfer surface temperatures. Operational experiences have confirmed that the HERB concept is possible to realize without endangering the mills availability.

New ways to produce more electricity have been introduced during the years. However, all the easy ways to enhance power production have been adopted and to be able to further increase the power-to-heat-ratio of recovery boilers may include high-risk measures.

High-temperature corrosion is mainly limiting the increase of steam outlet temperatures. Therefore, efforts have been put to overcome material issues in kraft recovery boilers. The Finnish Recovery Boiler Committee has also been active in promoting material studies and material research in different areas. The cooperation between boiler suppliers, mill operators, as well as with research institutes and universities, has led to practical solutions that have already been exploited in practical applications.

References

7. Salmenoja, K., 2000, Field and Laboratory Studies on Chlorine-Induced Superheater Corrosion in Boilers Fired with Biofuels, Academic Dissertation, Åbo Akademi University, Turku, Finland.
Progress in the field of kraft recovery boiler modeling is assessed by retrospectively looking at the proceedings of the 1991 Timberline Colloquium on Recovery Boiler Modeling (1991). The focus being on: the players involved then and now; the extent to which gaps have been closed since this colloquium and progress (or lack thereof) that has occurred since the time of this meeting.

The 1991 Timberline Conference was the first large gathering of those interested in developing kraft recovery boiler CFD capability, using CFD models and validating the results. It was a coming of age of this technology that had its infancy in the late 1980s.

Organized by Weyerhaeuser and B&W, two early leaders in this development activity, the conference had 51 attendees. I will delve a bit more into the attendees and their affiliations later in the paper.

Before diving into this topic we need to ask: What is the intent of this retrospective? I believe a proper study of history can provide valuable insight. The following are a few quotes that I borrowed from the American Historic Association (1985).

> . . . the changing perspectives of historical understanding are the very best introduction we can have to the practical problems of real life.

Clearly we need careful reflection about, and search for, enduring patterns and critical turning points in the past, for these are the historical facts that everyone needs to know ...

... ignorance of history--that is, absent or defective collective memory--does deprive us of the best available guide for public action...

This gives me my cue on how to go about this presentation: how has our understanding of CFD for kraft recovery boilers changed in the intervening time, what does this tell us about the problem of modeling, verifying and using CFD models; can patterns be extracted from the application of this technology that we can learn from and guide us moving forward; and how can this presentation be best used to retaining this knowledge so we can be guided going forward, so that this valuable tool can continue to become more useful.

I would be remiss in not mentioning the location, just outside of Portland, Oregon; the Timberline Lodge is located above the tree line on Mt. Hood, a dormant volcano in the cascades range. The lodge was completed in 1938 by the Works Progress Association (WPA). Many of you may have unwittingly seen footage of the lodge in the movie “The Shining” (red rum, red rum…). One of the snowiest places on earth it averages 14 meters per year. I encourage anyone visiting the Portland area to make the trek up to the lodge and stay at least one night. An old photo taken in 1943 is shown in Figure 1.
So let’s look back 23 years, before some of the audience was born and when most of us had far less gray hair.

Attendees and affiliations
As mentioned previously Weyerhaeuser and B&W were the organizers of the Colloquium. The introduction to the colloquium was given by Denny Hunter and Joe Barsin. Denny has recently retired from Weyerhaeuser. Most recently he was CTO at Catchlight Energy, the Weyerhaeuser-Chevron Joint-Venture for biofuels development. Joe Barsin, a longtime B&W employee retired a number of years ago but still remains active as a consultant.

The two keynote presentations are very informative and were given by two very well known researchers: Dr. Rolf Collin of the Royal Institute of Technology (KTH) and Dr. Martha Salcedan at the University of British Columbia. Both of these institutions have continued active research into CFD development but with distinctly different directions. UBC developed their own code, using multigrid segmentation and advanced solvers, eventually spinning off a company, Process Simulations Limited that continues to provide modeling service on kraft recovery boilers and a variety of other pulp and paper process equipment. KTH based on subsequently published research has made extensive use of Fluent a commercial code as a basis for the development of useful sub-models. These two different pathways will be touched on again later in the talk.

The other theme that is also worth considering is that of physical flow modeling as a basis for the validation of CFD and also as a valuable troubleshooting tool in its own right. Rolf described a technique where acid-alkali reactions are used to simulate mixing as a way to predict NOx emissions on a utility boiler. This theme will also be touched on further.

The other early pioneers on the attendee list included: Dr. Tom Grace, who led the development of the first comprehensive CFD model at the Institute of Paper Chemistry in the 1985-1989 timeframe. Two of his team members were in attendance, myself then representing ABB, and Allan Walsh, representing the J.H. Jansen Company. Allan continues to work in the field to this date; Woody Fiveland was also present, he was working for B&W, another company that has successfully developed and maintained their own CFD models to this date. Rick Wessel has long since taken over Woody’s efforts at B&W; Tampere University represented by Reijo Karvinen and Tampella represented by Pepka Siiskonen were already active in sub-model development using Fluent.

There were no representatives of Fluent at the meeting, but there were a number of end users of the commercial code, Gotaverken, Ahlstrom, Tampella, Jansen, ABB and perhaps some others. I will touch on Fluent’s role in kraft CFD development a bit more later on.

I’ve attempted to describe the attendees based on four different categories at the time of the meeting:

- CFD model user, CFD model developer, Validators – interested in proving value of CFD modeling, and other interested parties
- CFD Model Developers – IPST, ABB, Jansen, B&W, KTH, UBC, Tampere University of Technology, BYU (for Utility boilers mostly)
- CFD Model Users – Gotaverken, Ahlstrom, Oy Polyrec, Chemrec, Tampella (all using Fluent) Validators – Paprican, Quest Integrated, Sandwell, Weyerhaeuser (also a user of the UBC code), Advanced Fuel Research
- Interested parties - Longview Fiber, University of Toronto, U.S. DOE, International Paper, Åbo Akademi University, James River, Kimberly Clark, Swedish Pulp and Paper Research Institute. None of these attendees presented at this meeting. Within this group are two academic organizations (The University of Toronto and Åbo Akademi University) that have become critical contributors to model development, taking over from IPST. I believe some of the catalyst for taking on these roles was provided by this colloquium.

The topics

I will not address all of the individual presentations, but rather just touch on some of the highlights.

The combustion fundamentals work highlighted research on the burning properties of black liquor a topic that has been a key research topic to this day. Many PhDs have been received in an effort to fully examining this topic. A full understanding of these fundamentals is essential if accurate predictive CFD models are to be developed. A vital partnership exists between these developers of fundamental models suitable for CFD application and those using CFD to predict recovery boiler operation. The need for this partnership was recognized very early in the development of kraft recovery boiler CFD models.

This session ended with a panel discussion on char bed combustion. What was most interesting in this session was the discussion for a need for a dynamic char bed model that could predict the influence of operating parameters on char bed shape. It took another 17 (!) years to develop this type of model as described in a recent paper by Engblom et al. (2008).

The next session on the physical modeling of recovery boilers is a research area that most young engineers are probably not very familiar with. Before the rise of CFD, physical models were the only tool for predicting gas flows and mixing in combustion equipment. Early in the development of recovery boiler CFD models, validation of CFD results versus physical modeling results was an active research area. It was this work that allowed us to gain confidence in the CFD results, and in some case grave doubts. There are still some cases, such as very complex geometries, where only recently has CFD modeling advanced sufficiently to replace the utility of physical models.

In a subsequent panel discussion on the role of CFD on recovery boiler design the remarkable fact that B&W has been doing computational flow modeling since 1971 was mentioned. Some early kraft recovery boiler modeling results are shown in Figure 2. ABB, Ahlstrom (some early results shown in Figure 3), Tampella and...
Gotaverken also presented examples of CFD being used for recovery boiler design, some of the earliest references to the work of recovery boiler vendors in this field. These modeling efforts have continued to this day; the players have new names though, Metso (Valmet now!), Andritz and Alstom. It has been a very interesting history of recovery boiler manufacturers, but that is a topic for another day.

The next session on computer modeling of recovery boilers had a paper from Bob Horton of IPST, Bob led the modeling effort at IPST in the early 1990’s. Work was completed on a DOE project focused on improving droplet modeling and char bed modeling in kraft recovery boilers and integrating this work into the Fluent code. Martha Salcudean also presented a paper in this session that described the innovative work that was going on at the University of British Columbia at this time. They were using a code called Teach, that used high order differencing schemes and multi-grid techniques, improvements that would be adopted by commercial codes. Woody Fiveland of B&W then presented cold flow modeling results using FORCE a very early version of the (COMO-PR™) code that they have extensively developed since this time for kraft recovery boiler modeling applications. The last session on validation presented a few ideas on how to take in-situ measurements in a recovery boiler. It is unclear if either of the techniques: acoustic Doppler, or FT-IR have a recovery boiler. It is unclear if either of the ideas on how to take in-situ measurements in the last session on validation presented a few improvements in the early code development activities in this field at both of these institutions. Contact at this meeting certainly played a role in these efforts;

3. A number of topics were not even discussed in this meeting including simulation of soot-blower jets, modeling of flame deposition. Modeling of flame formation and modeling char bed growth were on the wish list but no efforts had been started at this time;

4. We have made significant progress since this meeting in a number of areas: validation, using CFD as a design tool, using CFD as a troubleshooting tool, modeling gaseous emission levels – NOx, CO, O2, and carry-over predictions;

5. There is a surprising continuity of players in this field. Many of the names from this conference are still active in the field. A number of new players have entered including the University of Toronto, Aalto University, Åbo Akademi University, Tampere University of Technology, and Umeå University.

Conclusions

1. Two valid paths of code development have been proven: build your own code (e.g. PSL, B&W and using a commercial code (e.g. Andritz, Valmet, Jansen). The second method has the advantage of being better able to support the inclusion of user defined sub-routines as the work product from others and in being able to rely on the software vendors to implement improvements to the general code. The “build your own” approach allows for possible competitive advantages in the quality of results and the control of the overall code. History has thus told us that there is a place for both of these approaches. Thus any user subroutine should be available as both user defined subroutines and as descriptive algorithms that can be then adapted by the do-it-yourself developers;

2. Academic organization have played a key role in sub-model development (usually freely available), the commercial code users can more easily benefit from these “open-sourced” models. This synergist relationship has many benefits and must be supported going forward;

3. Academic organizations need sources of funding in order to play this role. In the U.S. the DOE played this role, in Finland the support of Tekes has been vital.

4. What we did not even see in 1991 are now active areas of code development, not really a surprise but reassuring. Additional novel modeling applications must be pursued. One such idea is the ability to model growth and removal of deposits by sootblowers;

5. Validation is still elusive, some progress has been made but more work needs to be done. Getting validation data from an operating recovery boiler is a challenge and we need to continue to pursue means to do this.

On final point is that I have a copy of the proceedings from the 1991 Timberline Colloquium, I would be happy to make additional copies for anyone interested. Please contact me via e-mail if you would like a copy.

References


Black liquor gasification was proposed as early as in the 1960s as an alternative to the conventional Tomlinson Recovery Boiler for recovery of energy and chemicals from black liquor. The black liquor gasification based recovery process has the following potential comparative advantages (Whitty 2009):

• Elimination of the smelt-water explosion risk in a recovery boiler
• Elimination of malodorous compounds
• Improved power efficiency by using integrated gasification and combined cycle power generation
• Increased pulp production and increased pulp quality by utilization of split sulfidity pulping that is made possible by the natural separation of sulfur and sodium in a black liquor gasifier
• Improved control of the sodium-sulfur balance
• Possibility for efficient production of second generation motor fuels and high added value chemicals from sustainable forest biomass
• The historical development of black liquor gasification has been described by Whitty (2009) and the interested reader is referred to that paper and to the paper by Whitty and Verrill (2004) for more details. The conclusion in 2009 was that the future of black liquor gasification looked promising and that the high temperature, air/oxygen-blown entrained-flow gasifier with a direct quench.

The review is divided into sections about pilot scale experiments, durability of containment materials and mill integration.

The DP-1 pilot plant
The construction of the DP-1 pilot plant in Piteå, Sweden (Figure 1) started in 2004 and the first hot experiments were made in September 2005. The gasifier is an oxygen-blown entrained flow gasifier that operates at an internal pressure up to about 30 bar. The nominal black liquor flow rate is 20 tons dry solids per 24 hours and this corresponds to a thermal power of about 3 MW with the standard black liquor (app. 73% wt dry solids) from the neighbor pulp mill. The typical process temperature (as measured by the process thermocouples) needed for full carbon conversion is about 1050 °C and the corresponding oxygen equivalence ratio is in the range 0.3-0.4. The operating temperature is well above the

In this chapter the research on entrained flow gasification of black liquor during the last ten years will be summarized. Most of the research has been carried out within the framework of two Swedish research programs called BLG-1 (2004-2006) and BLG-2 (2007-2010) and within the EU 7th framework project BioDME. The gasifier design around which this research has been performed is the so-called Chemrec technology, which is an evolution of the original invention by Kignell (1989). The current Chemrec process is a slagging, oxygen-blown entrained flow gasifier with a direct quench.
melting point for the spent pulping chemicals and the resulting viscosity is very low so that any material that ends up on the hot reactor wall will form a liquid film that will flow out of the reactor lower exit. Residues that are suspended in the gas are also molten at this temperature.

The reactor pressure vessel is lined with refractory material consisting of two layers, a hot face with fuse-cast material with high resistance to chemical attack and one back-up layer with higher thermal insulation. The gas and molten salts that flow out of the hot reactor are quench-cooled with several spray nozzles that can be fed with water and condensate from the gas cooler. All or part of the spray will be evaporated until the gas becomes saturated with steam. The gas and molten salts that flow out of the reactor are quench-cooled with several spray nozzles that can be fed with water and condensate from the gas cooler.

After quench cooling and coarse removal of smelt droplets the syngas is fed to a syngas cooler operating in counter current mode. The syngas, which at this point is saturated with steam, will gradually be cooled in the syngas cooler. During this process the moisture will collect on particles in the syngas and on the heat exchanger surfaces. In the pilot plant the gas cooler is a tube-and-shell heat exchanger with two tube packages separated by a plenum chamber approximately at mid-height. In a full-scale plant the syngas cooler would instead be a heat recovery steam generator (HRSG) that would recover a significant fraction of both latent and sensible heat from the syngas and thereby improve the overall efficiency of the plant.

Chemrec AB, who holds several patents for the process, made the design of the DP-1 gasifier. The black liquor to the pilot plant comes from the neighboring pulp mill in Piteå, owned by Smurfit Kappa Kraftliner, through a pipeline that is connected to the mill’s black liquor evaporation plant. The green liquor from the gasifier is pumped back to the mill through a parallel pipeline. The pulp mill also provides medium pressure steam for preheating of black liquor and other purposes.

The pilot plant has several hundred sensors/actuators and an industry grade computerised control system that records all parameters, including the syngas composition measured with an on-line GC. The pilot plant design is identical to a full-scale industrial gasifier with the exception that there is a lack of redundant systems that would make it possible to do routine maintenance without shutdown of the plant. The limiting factor at present is the green liquor return system that has to be cleaned from fouling with inorganic deposits with three-week intervals. Two operators can run the plant safely.

During the break-in period during the first year of operation a number of issues typical for start-up of a new process had to be resolved, e.g. replacement of pumps and flow meters that did not perform according to the requirements. Other than these rather trivial problems the major effort was spent on optimisation of the burner nozzle to obtain a stable flame and good carbon conversion. At present, in April 2014, the plant has an accumulated run time in excess of 25000 hours and it is routinely operated 24/7 in three-week periods (Landälv et al. 2014).

Pilot scale experiments

The main goal with the pilot plant experiments in the DP-1 plant was to run the plant in the same way as an industrial gasifier to prove that the technology was reliable and mature enough to be implemented in a full-scale commercial plant. Since the plant, due to budgetary reasons, was built without redundant systems the possibility for continuous operation was somewhat limited. The goal for operation was therefore set to achieve at least three weeks of continuous operation without interruptions. This was achieved for the first time in the fall of 2007. Another goal was to gradually increase the load and to operate the plant at its design capacity and pressure and this was achieved the same year. After these achievements the goal was to maximize the operational time during the rest of the program to make it possible to expose any unexpected long term problems due to build up of trace elements and to quantify the material degradation/need for maintenance. In June 2013 the accumulated operation time had surpassed 20000 hours (Figure 2). In addition to the industrially motivated activities mentioned above, the plant was also used for scientific research that is described in the following.

Closure of the material and energy balance for the DP-1

A key measure of the goodness of pilot scale experiments is how well the mass and energy balances can be closed, based on direct measurements of the relevant parameters. In the present case, in order to analyze the data, the following assumptions had to be made:

- The amount of dilution water entering the system is unknown. The flow rate was therefore adjusted to close the water balance around the system. The resulting value was typically around 700 kg/h, which can be compared to the black liquor flow rate that was around 900 kg/h in the experimental campaign for which the balances were made.
- The water formed by the reactions in the reactor was also unknown as a consequence of the bullet point above. The formed water was assumed, based on a theoretical estimate, to be 100 kg/h.
All other flow rates were taken from direct measurements. The system boundary for the system is defined in Figure 3.

A detailed mass and energy balance was done for the system defined in Figure 3 in an experimental campaign in March 2009 (Granberg et al. 2009). Four independent measurements were done, each separated by around 24 hours from the previous one. Mass balances were checked for the total flows and for each major element. The mass balance closures were in most cases within 10% difference between inflow and outflow. However, for nitrogen the error was 29-28%. The most likely explanation of this discrepancy is that nitrogen was bubbled through the green liquor to enhance mixing and that some of the nitrogen was absorbed by the green liquor and was therefore unaccounted for. This explanation is further strengthened by direct measurements of the dry gas from the green liquor flashtank that showed that it consisted mainly of nitrogen and hydrogen.

One important result from the mass balances is the sulfur-sodium split that results in the transfer of one important result from the mass balances is that showed that it consisted mainly of nitrogen that was absorbed by the green liquor and that some of the nitrogen was bubbled through the green liquor to enhance mixing and that some of the nitrogen was absorbed by the green liquor and was therefore unaccounted for. This explanation is further strengthened by direct measurements of the dry gas from the green liquor flashtank that showed that it consisted mainly of nitrogen and hydrogen.

The gasification process is a non-equilibrium (Backman 2010). Hence, it can be concluded that the gasification process is a non-equilibrium process for the inorganics.

Syngas composition

The syngas composition from the DP-1 gasifier, after the gas cooler, was continuously measured with an on-line process GC. The data was automatically stored in the process-monitoring database for off-line analysis. In order to investigate the influence from quenching and gas cooling on the syngas a set of experiments were performed in which the syngas was instead sampled from the hot reactor. The sampling was done with a specially designed water-cooled probe that could be mounted in different positions (Wiinikka et al. 2010). The cooling rate for the syngas that is sampled with the probe should be of the order 1000 K/s and the gas composition at the sampling point is therefore efficiently “frozen”. The samples were stored in a sampling pressure vessel that could be disconnected for offline analysis with a calibrated GC. Using this probe a set of experiments with variations of process parameters were done (Carlsson et al. 2010). A typical gas composition from these experiments can be seen in Table 1. Notice, that the measured change in most of the components before and after the quench are within the experimental uncertainty but that the COS concentration is significantly reduced after the quench.

The parameter study was done by changing the system pressure, oxygen to black liquor equivalence ratio \( \lambda \), black liquor flow rate to pressure ratio and black liquor pre-heat temperature. It was found that all of these parameters had a significant effect on the product gas composition and other important process characteristics (Carlsson et al. 2010). The main conclusions from the study are:

- The bulk composition of the product gas is mainly determined by the water gas CO-shift reaction and thus, by the operating temperature which to a large extent is controlled by \( \lambda \).
- Increased system pressure promotes \( \text{H}_2\text{S} \) in the gas.
- Increased \( \lambda \) suppresses the amount of \( \text{CH}_4 \) in the gas.
- The amount of analyzed carbon containing gases increase with decreased black liquor flow rate to pressure ratio.
- At constant pressure, the heating value of the gas increase with increased black liquor flow rate to pressure ratio.
- Increased black liquor pre-heat temperature suppresses \( \text{CH}_4 \) and \( \text{H}_2\text{S} \) content in the gas.

The characteristics of the gasifier were further investigated in another experimental campaign in which the influence from the cooling rate on the product gas composition was investigated. The cooling rate was varied by changing the flow rate of water to the quench (Wiinikka et al. 2012). It was found that the hot reactor gas composition prior to the quench could either be preserved (high cooling rate) yielding the same final gas composition after the quench as in the hot reactor or shifted (low cooling rate) towards a higher concentration of \( \text{H}_2 \) and \( \text{CO}_2 \).

The conclusions from this study are in line with the previous results but with added insight into the influence from the quench:

- The system pressure, \( \text{O}_2/\text{BL} \) flow ratio, and the primary spray flow affect the final gas composition of \( \text{CO}_2 \), \( \text{CO} \), and \( \text{H}_2 \) after the quench. The system pressure and \( \text{O}_2/\text{BL} \) flow ratio also affect the concentrations of \( \text{CO}_2 \), \( \text{CO} \) and \( \text{H}_2 \) inside the hot reactor.
- The primary spray flow rate/load (mass flow of black liquor and oxygen) ratio has a critical value of about 0.6 below which concentrations of \( \text{CO}_2 \), \( \text{CO} \), and \( \text{H}_2 \) are significantly changed in the quench.
- For high primary spray flow rate/load ratios, the temperature is reduced adequately fast to prevent any significant influence from the water–gas shift reaction and therefore the gas concentration after the quench is nearly the same as in the hot reactor.
- For low primary spray flow rate/load ratios, the chemistry in the quench is highly influenced by the water–gas shift reaction and the gas composition after the quench is shifted to more \( \text{H}_2 \) and \( \text{CO} \) and a smaller amount of \( \text{CO}_2 \) than in the hot reactor.
- For high primary flow rates, \( \text{CO}_2 \) absorption can become significant.

A common problem area in biomass gasification is tar in the product gas. The relatively problem free operation of the DP-1 gasifier (very little fouling on cold surfaces) shows that the tar content is low but in order to quantify the amount of tars Johansson et al. (2013) have made a directed measurement. The measurements were done both according to the CEN Tar Measurement Standard and with a solid phase adsorption (SPA) method. The tar content was found to be about three orders of magnitude lower than from low temperature fluidized bed gasification of forest biomass, 4-9 mg/Nm$^3$ with the CEN standard method and slightly higher with the SPA method. Approximately 50% of the total tar content was found to be naphthalene.

Other trace components were also investigated by Öhrman et al. (2012). The particle concentration in cooled syngas was measured with a particle impactor and the particle concentration was found to be very low (Figure 4). As a reference, good wood combustion yields a flue gas that has particle loading that is about two orders of magnitude larger (in the vicinity of 10 mg/Nm$^3$).

Eleven different elements and compounds were also analyzed using impinger bottles through which the syngas bubbled. Out of the 11 elements and compounds that were analyzed only two, Cl at 3 ppm and NH$_4$-N at 100 ppb, were found in concentrations above the detection limit. Chlorine is a potentially problematic element

![Figure 3. System boundary for the DP-1 material balance.](image-url)
The concentration of sodium hydroxide, sodium sulfide and sodium carbonate. The conclusions from the study are that the separation properties for the green liquor and the total concentration of the produced white liquor are almost identical between the two cases. Moreover, it was found that the causticizing efficiency was almost the same for gasifier produced green liquor and the conventional green liquor in spite of the significant differences in green liquor composition between the two cases and the fact that more reburned lime mud must be used to causticize the green liquor from the DP-1 gasifier.

One significant difference between a conventional recovery boiler that operates at atmospheric pressure and a pressurized gasifier that operates at a pressure around 30 bar is that the green liquor temperature will be up to about 100 K higher in the gasifier case before it is depressurized and cooled to below the boiling point. In addition, a significant fraction of the sulfur in the black liquor will in the gasifier case be transformed to gas phase as H₂S and possibly other sulfur compounds. In all, this means that there is a possibility that the formation of deposits on solid surfaces in the green liquor system will be different in the two cases. Bialik et al. (2010) have therefore done both theoretical and experimental work to assess the scaling risk. The theoretical work is based on a solubility model for sodium carbonate, calcium carbonate and pirssonite (Ulmgren et al. 1999) that was used to evaluate the scaling risk in green liquor from the gasification process. The model was first verified against samples from the DP-1 gasifier that were obtained under different process conditions. In this study, it was found that the green liquor composition was relatively insensitive to process variations when the process parameters were varied within their normal limits. The overall conclusion in the study by Bialik et al. (2010) is that the risk for pirssonite precipitation in gasification green liquor is relatively low.

After the study of Bialik et al. was done the DP-1 gasifier has been operated for a total of more than 20000 hours using optimized settings of the gasifier process variables (Landälv et al. 2014). The green liquor from the gasifier is continuously flashed and pumped back to the host pulp mill for mixing with the green liquor from the recovery boiler. The operational experience from this extended operating period is that there will be a slow formation of scaling on the components that are in contact with the green liquor but the deposits are easily removed by a standard acid wash approximately every three weeks.

As mentioned above, black liquor gasification leads to an increased demand for reburning of lime mud compared to chemicals recovery with a Tomlinson boiler. Several investigations have therefore focused on the possibility to reduce or completely remove the need for causticizing by adding a causticizing agent to the black liquor before it enters the gasifier. Nohlgren and Sinquefield (2007) presented results from experiments in a pressurized drop tube furnace in which black liquor with an additive of sodium borate was exposed to simulated gasification conditions. The conclusion is that the presence of CO₂ in the black liquor for a new gasification cycle. However, no auto-causticizing was detected and the conclusion is that the presence of CO₂ in the gasifier inhibits the auto-causticizing reactions under gasification conditions.

An alternative to borates for auto-causticizing is to use titanates instead. Sinquefield et al. (2010) have presented an experimental study similar to that by Nohlgren and Sinquefield (2007) and obtained slightly better results than for borate auto-causticizing. However, also in this case the inhibition of the reactions by CO₂ makes it unfeasible to use this method in a gasifier similar to the DP-1 where the operating pressure is around 30 bar.

**Mill integration**

Recovery of energy and chemicals from the black liquor is a necessity for a modern pulp mill, both from an economic and an environmental point of view. The industry standard is to use a so-called Tomlinson recovery boiler (Tomlinson & Wilcox 1939) for efficient recovery of energy and chemicals from spent pulping liquors. The main reason why this is so is that the recovery boiler can be tightly integrated with the rest of the pulp mill and provide the energy and the pulping chemicals that are needed for the pulping process thereby minimizing the need for additional fuel and make-up chemicals.

Larson et al. (2000) made a flow sheet analysis of several proposed black liquor gasifiers that were used for integrated gasification and combined cycle power production (IGCC) and compared the economics to that for a conventional recovery boiler. The conclusion is that the financial cost is about the same as for the recovery boiler but that the power production can be doubled to tripled. Hence, the power production cost will be about half that with Tomlinson-based technology.

After the turn of the century much of the interest shifted to the combination of black liquor gasification with syngas conversion into motor fuels and high added value chemicals. Consonni et al. (2009) made detailed mass-energy balance simulations and combined that with a financial analysis for seven pulp mill biorefinery process.
configurations, all of them based on an oxygen-blown, high temperature black liquor gasifier. Six of the alternatives also included a low temperature fluidized bed biomass gasifier for IGCC power production that was fully integrated with the gasification and syngas cooling section of the black liquor gasifier. Three different biofuels were considered, dimethyl ether (DME), FT liquids and mixed alcohols. The ratio of useful energy outputs (steam, power, fuels) to total energy inputs (black liquor, wood residuals, fuel oil) were in the range 66-74% compared to about 57% for a Tomlinson boiler based system. The estimated specific capital investment cost was found to be US$60000-150000 / barrel diesel equivalent per day which is about the same as for a much larger coal-to-liquids plant.

Petterson & Harvey (2012) made a similar study in which black liquor gasification based biorefinery alternatives were compared to recovery boiler-based pulping biorefinery concepts both from an economic and climatic point of view. It was found that black liquor gasification with DME production had the best economic performance for all the energy market scenarios that were considered. It was also concluded that the black liquor gasifier should, from an economic point of view, be supplemented by a solid biomass gasifier for additional syngas that can be used both for synthesis of additional DME and for power production.

Durability of containment materials

Black liquor is a very corrosive liquid and, regardless of the recovery technology, the material selection for components that are in contact with the medium must be done cautiously. For the recovery boiler, more than seven decades of development and industrial experience has led to material combinations that have an acceptable lifetime and safety level. For black liquor gasification the experience is much shorter but the experience from the Weyerhaeuser New Bern booster gasifier has yielded a good starting point for evolutionary development. Initially, the lifetime of the refractory lining of the reactor vessel in New Bern was disappointing (Keiser et al. 2007). After systematic development of the material solution and extended tests it was concluded that the optimized materials will have a lifetime of about two years for a gasifier that is continuously operated.

Conclusions

Pressurized, oxygen blown entrained flow gasification of black liquor has undergone a significant development since the turn of the century. The accumulated operating time of the oxygen blown DP-1 pilot gasifier exceeds 20000 hours (in May 2014 it is over 24000 hours) and the process is reliable and predictable. The syngas has very low tar content and is suitable both as a gas turbine fuel and as syngas for catalytic production of motor fuels and chemicals.

The process can also be integrated with existing pulp mills in a very efficient fashion that has the potential to improve the pulp mill profitability and reduce its carbon footprint by production of fuels that will displace fossil fuels at the same time.

References