ÅBO AKADEMI 100 YEARS;
RECOVERY BOILER RESEARCH HIGHLIGHTS

Mikko Hupa, Åbo Akademi

Recovery Boiler Research at the 100 years old Åbo Akademi

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Åbo Akademi, Turku, Finland

Introduction

Our university Åbo Akademi was founded in 1918, and had its first ca 40 students started their studies in the Spring 1919, exactly 100 years ago. We are very happy to have the Finnish Recovery Boiler Committee Conference organized here in Turku in connection with our 100 years anniversary. Chemical engineering has been one of the strong areas of our university since the very beginning, and a great number of our former students have in different positions been part of the development of the pulp and paper industry in Finland.

Black liquor combustion and the recovery boiler process have been an important research area at Åbo Akademi since almost 40 years. The purpose has been to support the development recovery boiler technology by providing deeper understanding of the chemical processes in the furnace and flue gases. Many challenges in boiler design and operation are connected to chemical process details, and these we have studied by a variety of laboratory tools, by theoretical calculations, and by measurements and sampling in operating boilers. This paper reviews our recovery boiler research by discussing the most important research techniques used during these 40 years.

Probes

The use of air-cooled probes to sample short term flue gas deposits has been one of our key tools to collect controlled information on the deposit formation and chemical composition of the flue gas dust in different locations in the boiler. By the probe samples – altogether in more than 40 recovery boilers around the world – we have learnt to understand the big differences in the amount and stickiness of the carry-over and fume particles under different conditions. The concept of the critical partial melting temperatures (T_0, T_{15}, T_{70} and T_{100}) has been very useful in explaining the differences in the behaviour of dusts and the role of the steep temperature gradient across the deposits.

Recently the deposit exposed to the temperature gradient was realized also in the laboratory set-up. This has shed more light to the different layers of the deposits and particularly the role of the migration of alkali chlorides in the temperature gradient.

Single droplet burning

It is known that different liquors behave differently when burned in the furnace. We started studying the liquor burning characteristics by burning suspended single liquor droplets in a laboratory furnace at well-defined conditions. Already a simple video recording of the burning droplets gave relevant parameters by which the liquor burning characteristics could be described. The most important was the characteristic swelling of the droplet during the devolatilization stage. The swelling tendency varied widely, from heavily swelling liquors with a volumetric maximum swelling by a factor 100 to completely non-swelling liquors.

Swelling strongly influences the burning rate of the droplet – the more swelling during devolatilization the faster burn-out time. Swelling also influences the droplet trajectories in the furnace, the amount of carry-over and the whole furnace behaviour. These changes due to the differences in droplet swelling could later be shown also by Computational Fluid Dynamics based furnace model calculations (See Figure 1). Till today we have data on the burning behaviour of more than 400 liquors.

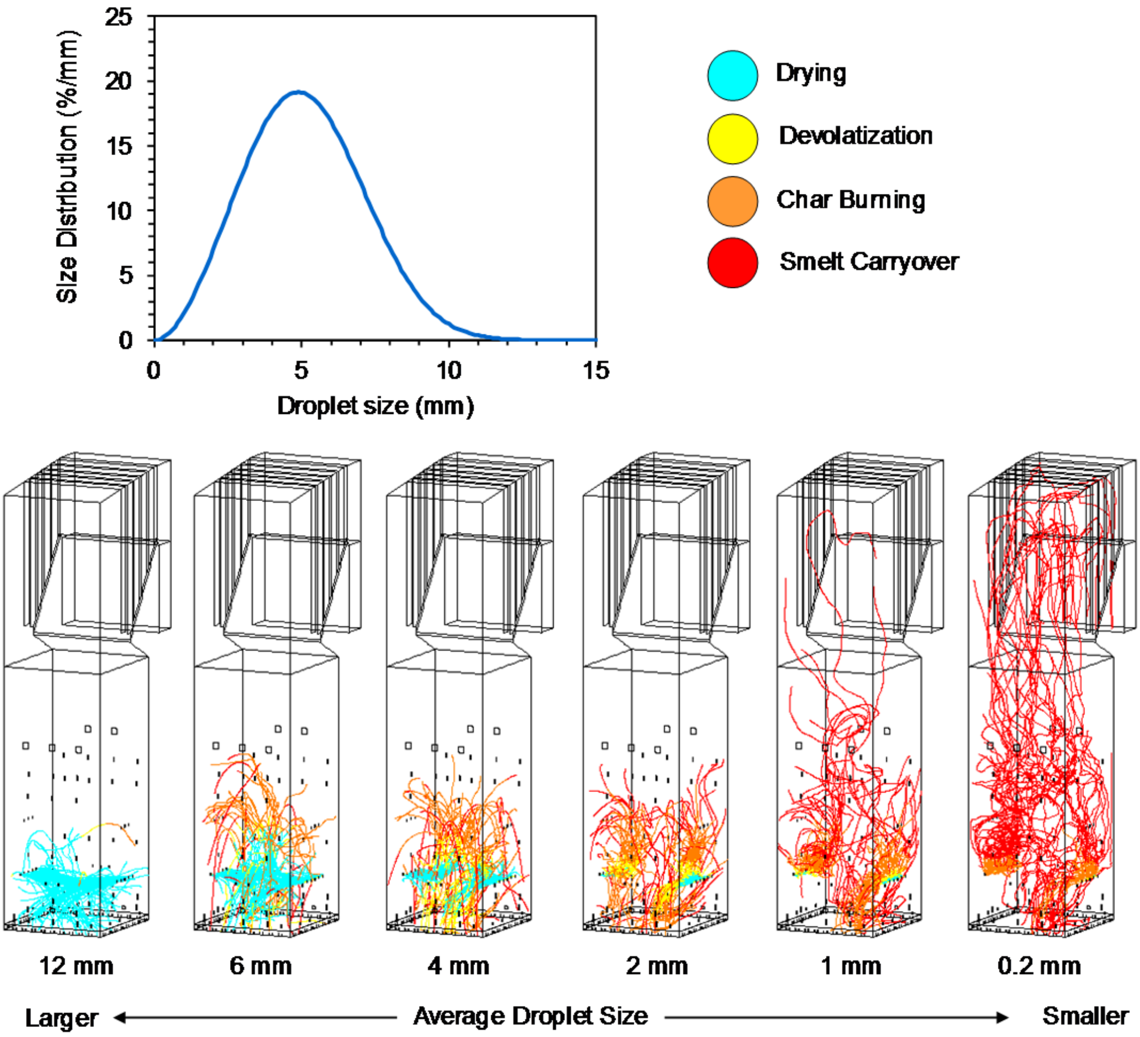

Figure 1. *Black liquor particle trajectories for drops with different initial diameters in a recovery boiler firing black liquor through five splash plate nozzles on each side wall at one level. Air distribution: 22% to primary, 43% secondary and 35% tertiary (Engblom et al, 2018).*

Nitrogen cycle

The single droplet test was later developed further with analysis of the flue gases produced by the burning droplet. By this technique we were able to establish the detailed reaction pathways of the organically bound nitrogen in the liquor during the burning. Part of this organically bound nitrogen in the liquor was released during the devolatilization stage and oxidized to NO. This fuel NO was further shown to be the main source to the total NO emission from the recovery boilers. The great surprise in this research was the finding that part of the liquor-bound organic nitrogen stayed in the final inorganic smelt. The compound in the smelt was later identified to be sodium cyanate, NaOCN.

The further fate of this smelt cyanate was a topic of several excellent Thesis projects at Åbo Akademi and today the picture is quite clear. In the green and white liquor the cyanate gradually reacts to form ammonia. This dissolved ammonia will be released from the recovery liquors into the gas phase – mostly during the evaporation of the black liquor. To what extent this gaseous ammonia will cause additional air emissions is dependent on the details of the recovery cycle.

Mill campaigns

To tie laboratory tests or modelling results to the real world, studies at operating recovery boilers are crucially important. We have participated in measurement and sampling campaigns at a number of boilers. In one of the most exciting campaigns - already more than 15 years ago - we wanted to study to which extent the flue gas fume and nitrogen oxides are formed by burning droplets in-flight or by burning on the char bed. We measured the fume and NO concentration in the flue gases by special continuous analysers over a short 2 min interruption of the liquor feed. This amazing test was done at two boilers – in both cases just before the scheduled Midsummer shut-down. The results were extremely interesting and showed how around 90 % of the fume and practically 100 % of the NO is formed from the burning droplets in-flight (See Figure 2).

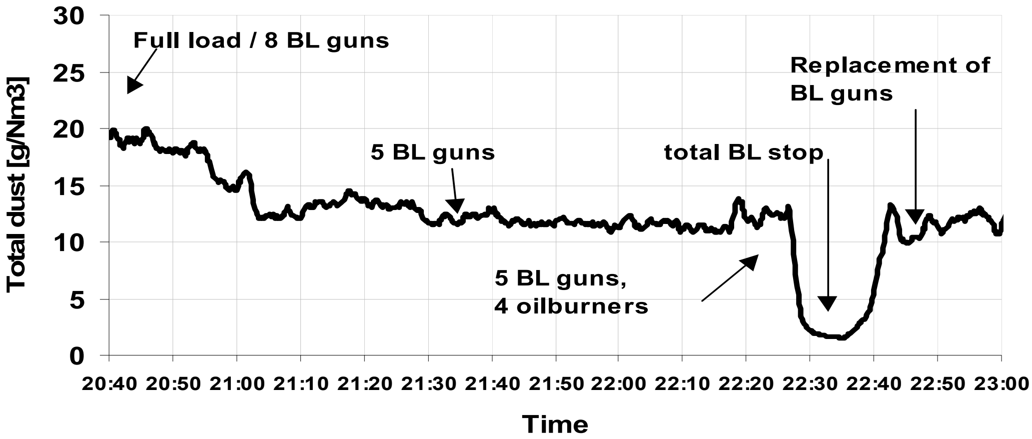

Figure 2. *Dust concentration in the flue gases during a campaign where BL firing was interrupted and replaced by gas for a period of ca 15 min (Tamminen et al 2002).*

Conclusions

The examples discussed show how solid scientific laboratory work combined with theoretical modelling can shed light to the complicated processes in black liquor combustion and that way help solving a variety of operational and design problems. Further, systematic measurements in operating boilers are of great value to test and confirm the results obtained in the laboratory.

Acknowledgements

Åbo Akademi thanks the Finnish Recovery Boiler Committee for the long and fruitful collaboration. Further, the ongoing strong support by the Åbo Akademi combustion research consortium companies Andritz Oy, Fortum Power and Heat Oy, International Paper Inc., UPM-Kymmene Oyj and Valmet Technologies Oy is highly appreciated.

SUOMEN SOODAKATTILAYHDISTYS
FINNISH RECOVERY BOILER COMMITTEE

Åbo Akademi

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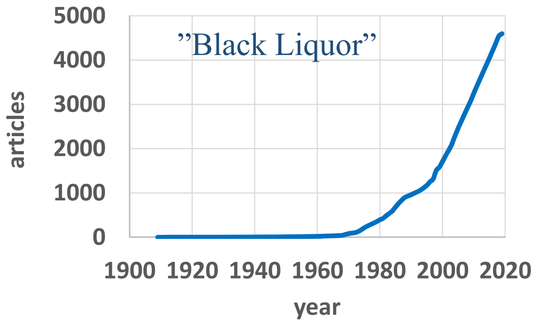
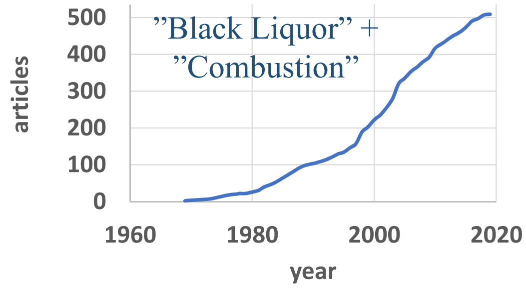
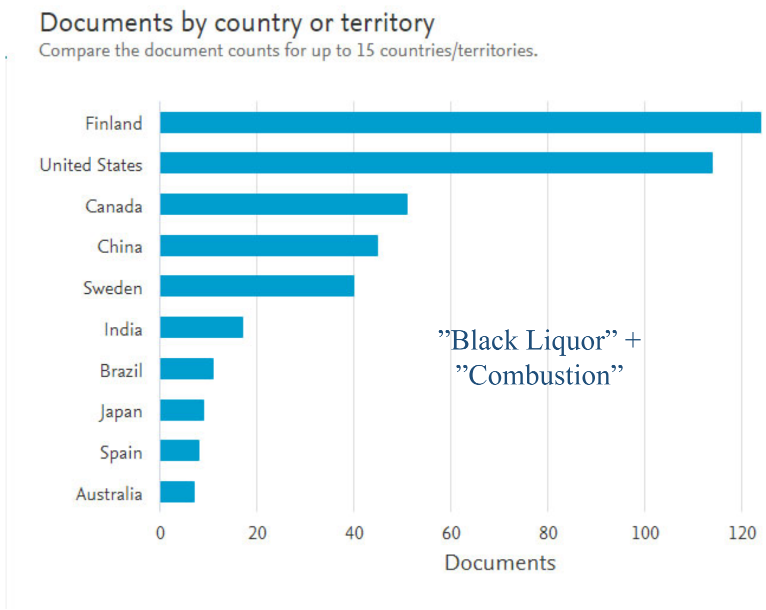
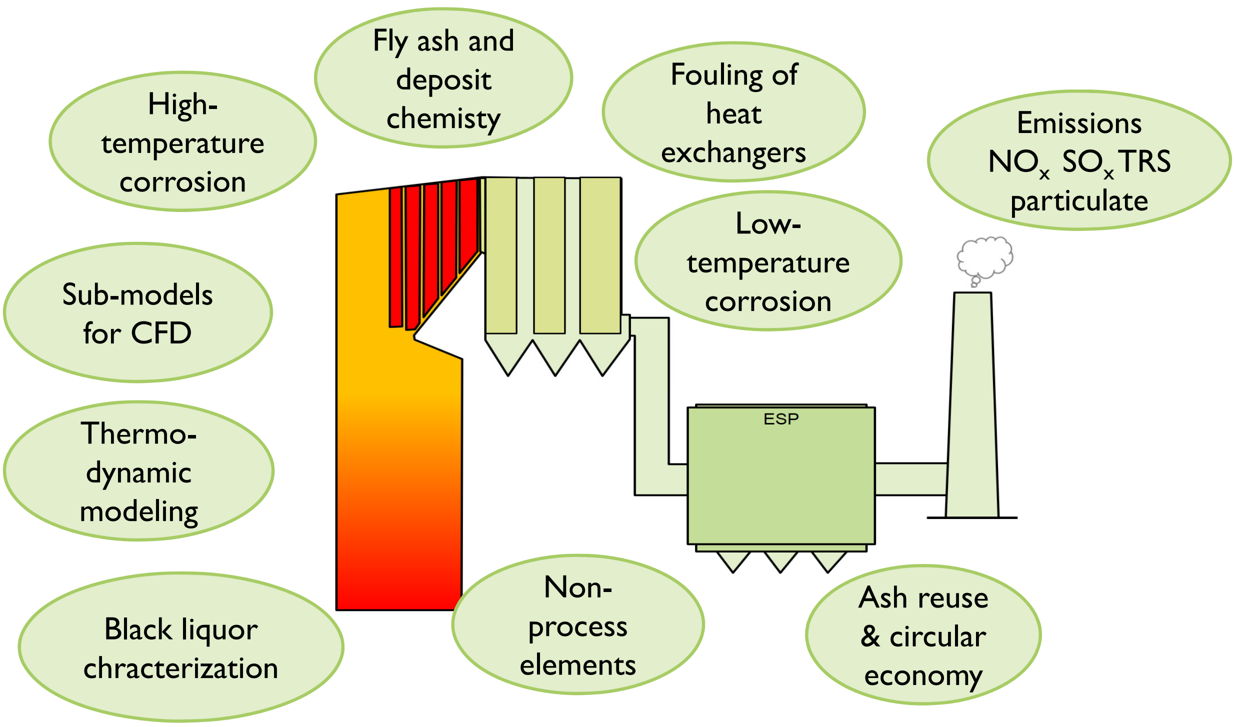
Scientific Literature on Black Liquor







Åbo Akademi Recovery Boiler Research Topics



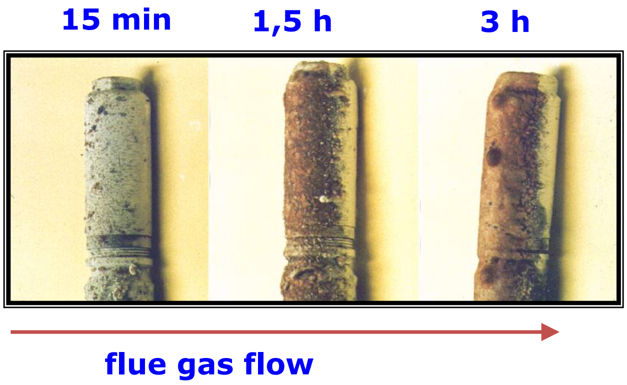
Research Approaches – Since 1980

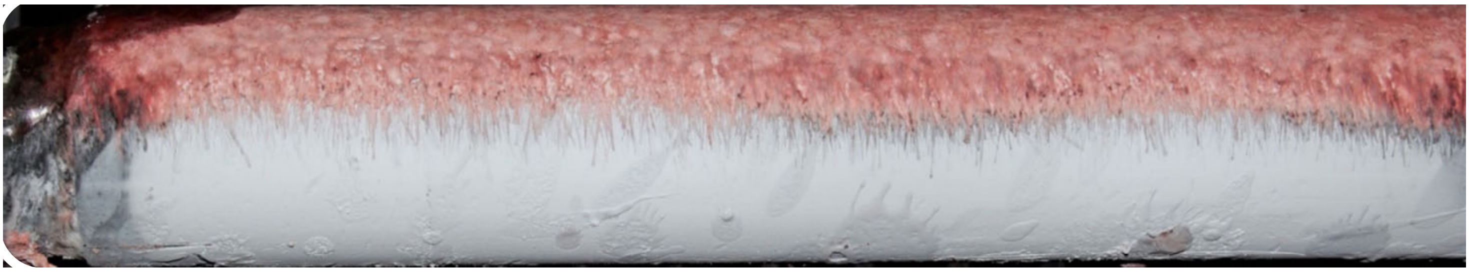
Research Approaches – Since 1980

- Deposit Probes
- Single Droplet Experiments
- Full-scale Measurement Campaigns

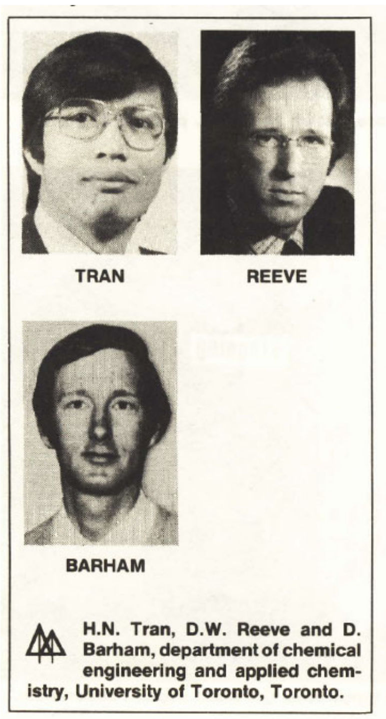
Probe samples

(Kemi Veitsiluoto 1980)

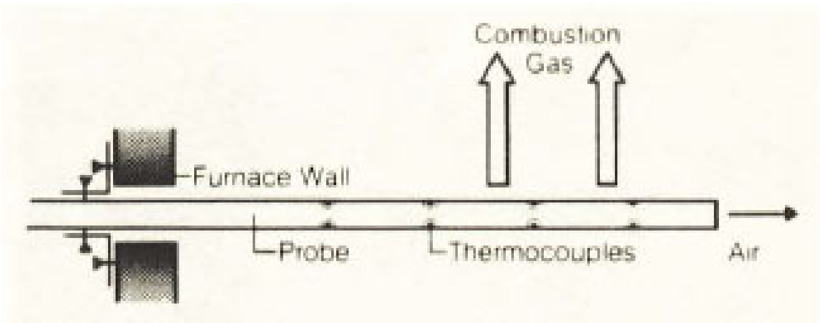




Probe Studies Elsewhere


TRAN
REEVE
BARHAM

H.N. Tran, D.W. Reeve and D. Barham, department of chemical engineering and applied chemistry, University of Toronto, Toronto.



- Air-cooled probe
- Above bullnose, before superheaters

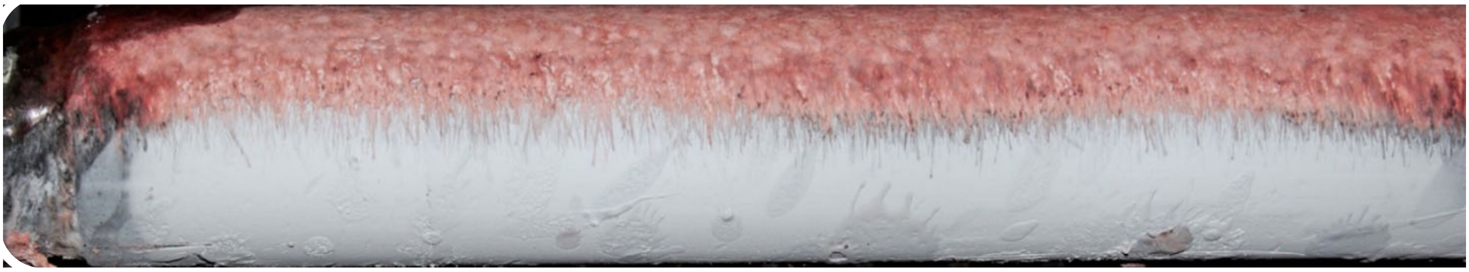
(Pulp and Paper Canada 84:1, 1983)

Probe samples
(Kemi Veitsiluoto 1980)

15 min 1,5 h 3 h

flue gas flow

- Carry-over and fume chemistry
- Amount of carry-over
- Molten surface (equilibrium thickness)
- Partial melting: T_0 T_{15} T_{70} T_{100}

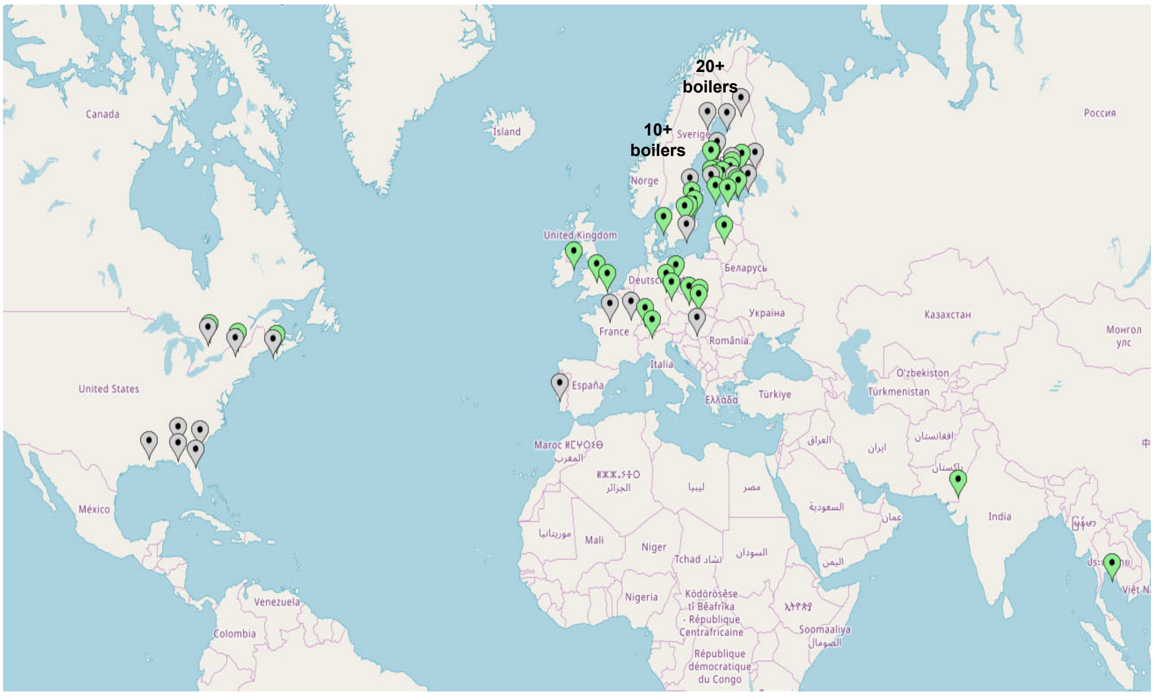


Åbo Akademi Probe Studies

- Kraft & Sulfite
- BFB, CFB, Grate, PF
- Smelters, Kilns, Engines

Åbo Akademi Probe Studies

- 15 countries
- 60 locations
- 100+ campaigns



Finland, Sweden, Poland, Ireland, UK, France, Slovenia, Lithuania, Germany, Austria, Belgium, Thailand, India, USA, Canada

Kraft & Sulfite

BFB, CFB, Grate, PF

Smelters, Kilns, Engines

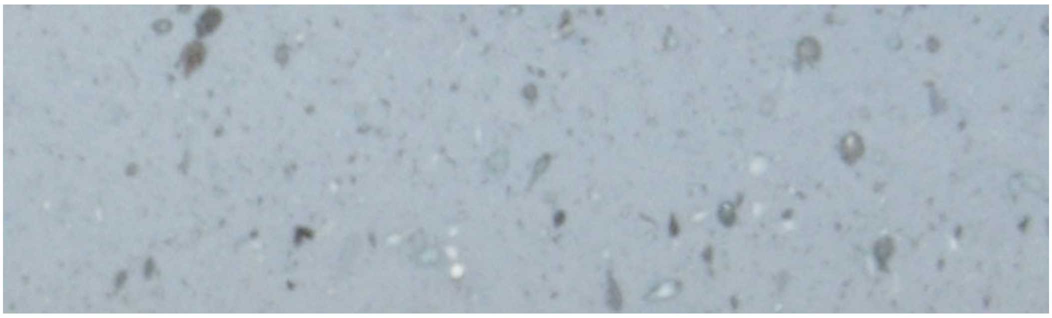
Uncooled Short-time Probe – One Minute Probe

Vähä-Savo, N., Yrjas, P., Laurén, T., Hupa, M., *JPPS* 36 (2011) 3-4, 143-150

Uncooled Short-time Probe – One Minute Probe

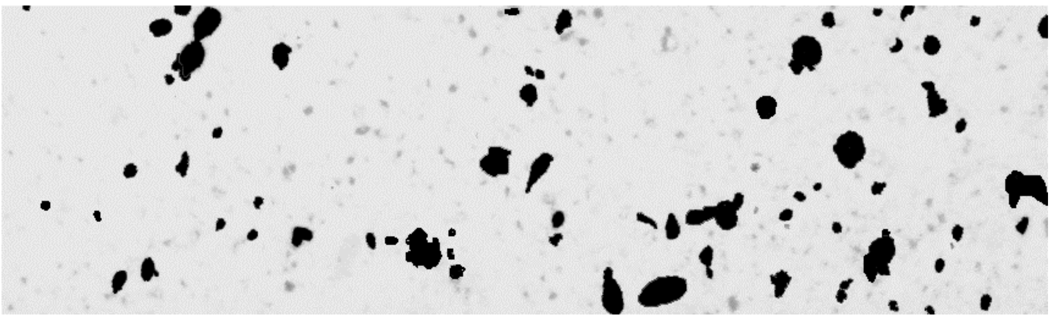
Vähä-Savo, N., Yrjas, P., Laurén, T., Hupa, M., *JPPS* 36 (2011) 3-4, 143-150

Short-time Carry-over Measurement



Vähä-Savo, N., Yrjas, P., Laurén, T., Hupa, M., *JPPS* 36 (2011) 3-4, 143-150

Short-time Carry-over Measurement



Vähä-Savo, N., Yrjas, P., Laurén, T., Hupa, M., *JPPS* 36 (2011) 3-4, 143-150

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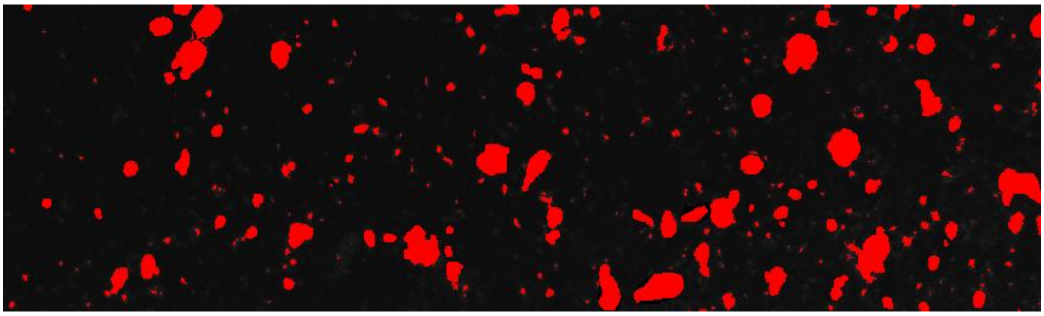

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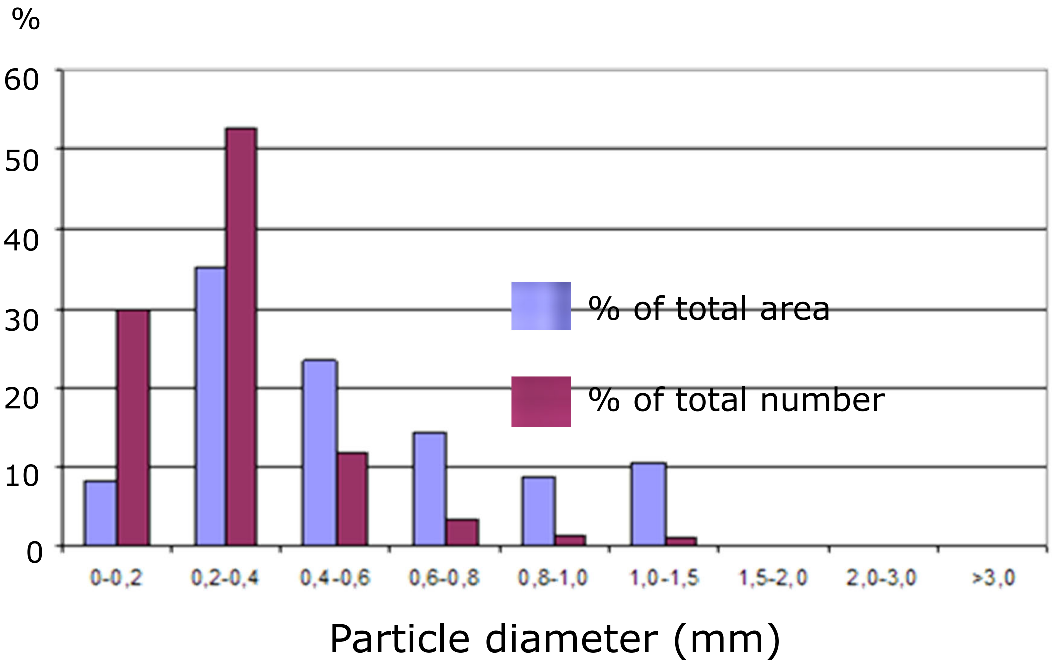

Vähä-Savo, N., Yrjas, P., Laurén, T., Hupa, M., *JPPS* 36 (2011) 3-4, 143-150

Deposit Probe with Temperature Gradient

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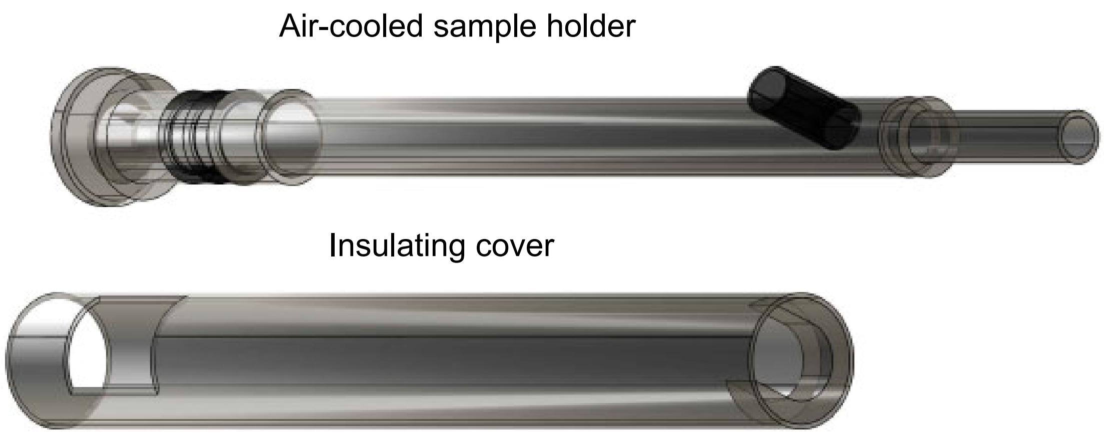
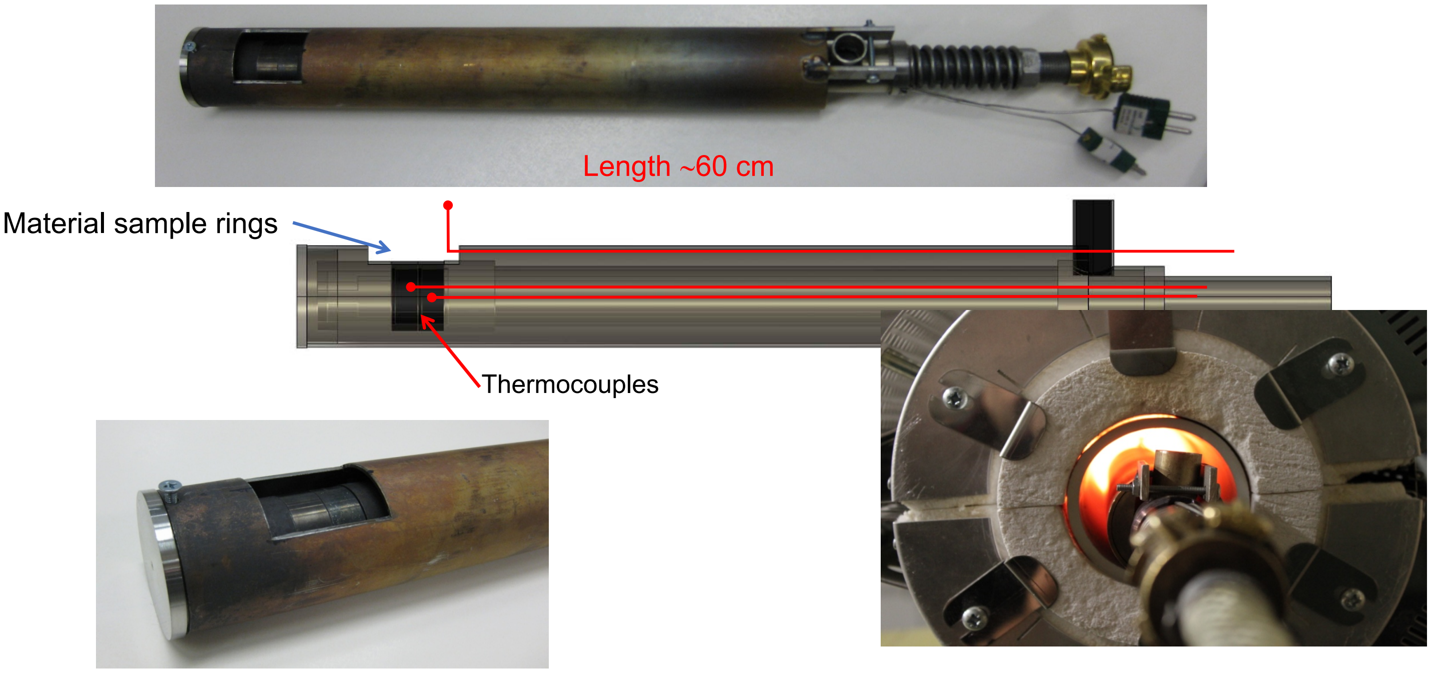
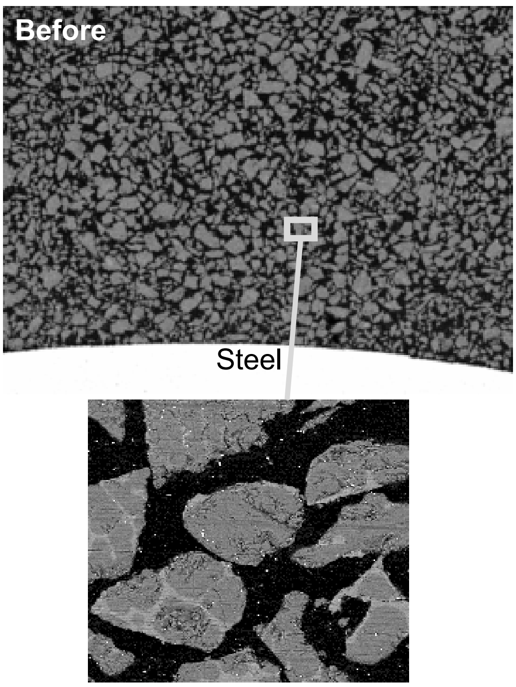


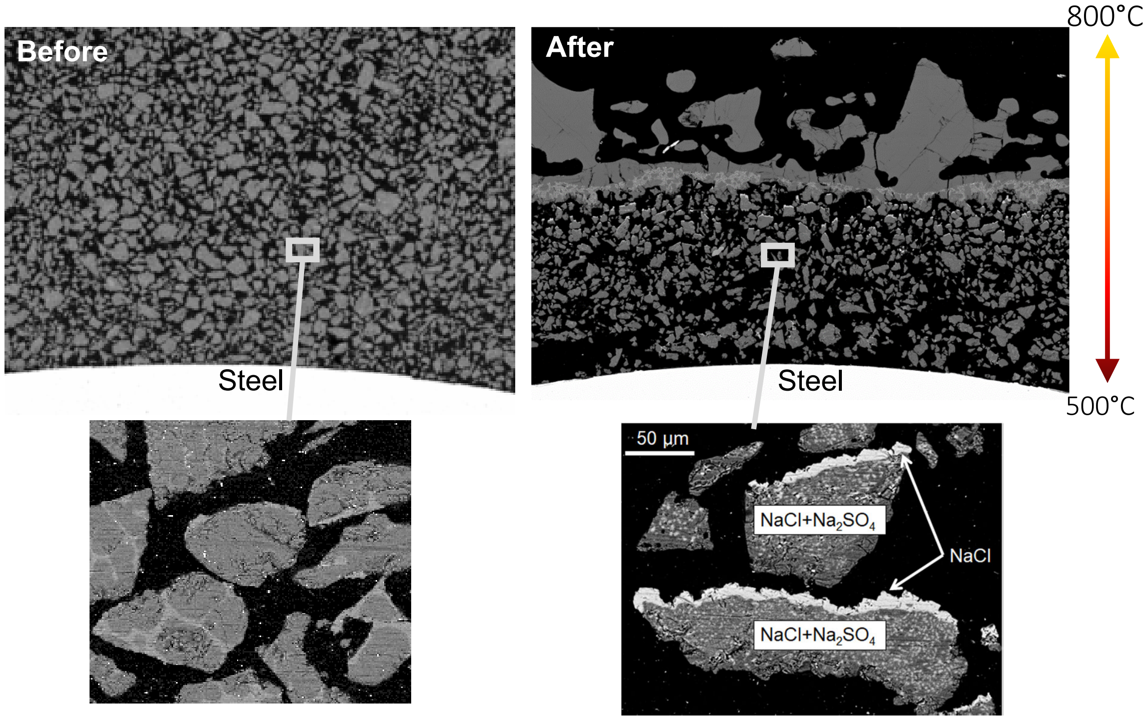
Deposit Probe with Temperature Gradient



Sulfate/Chloride Deposit in Temperature Gradient

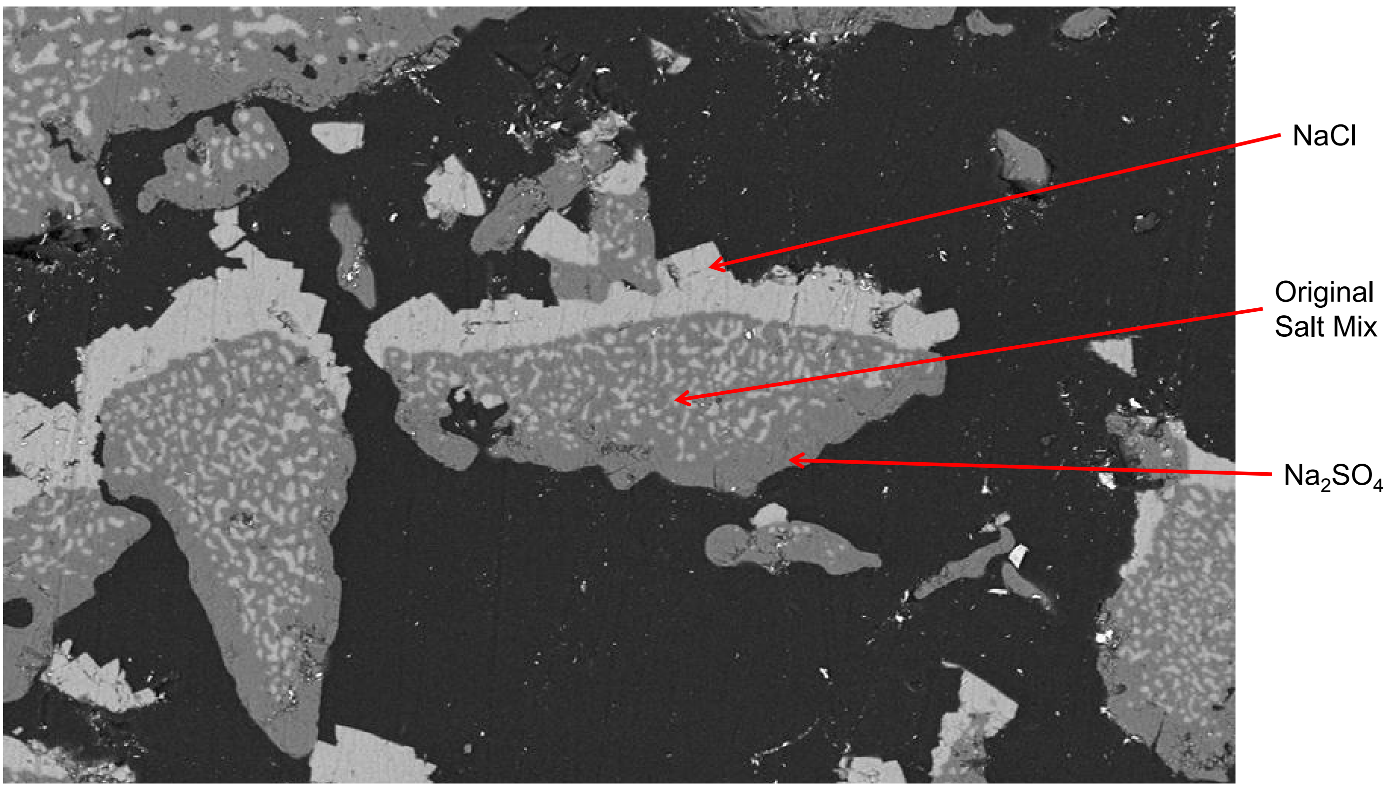


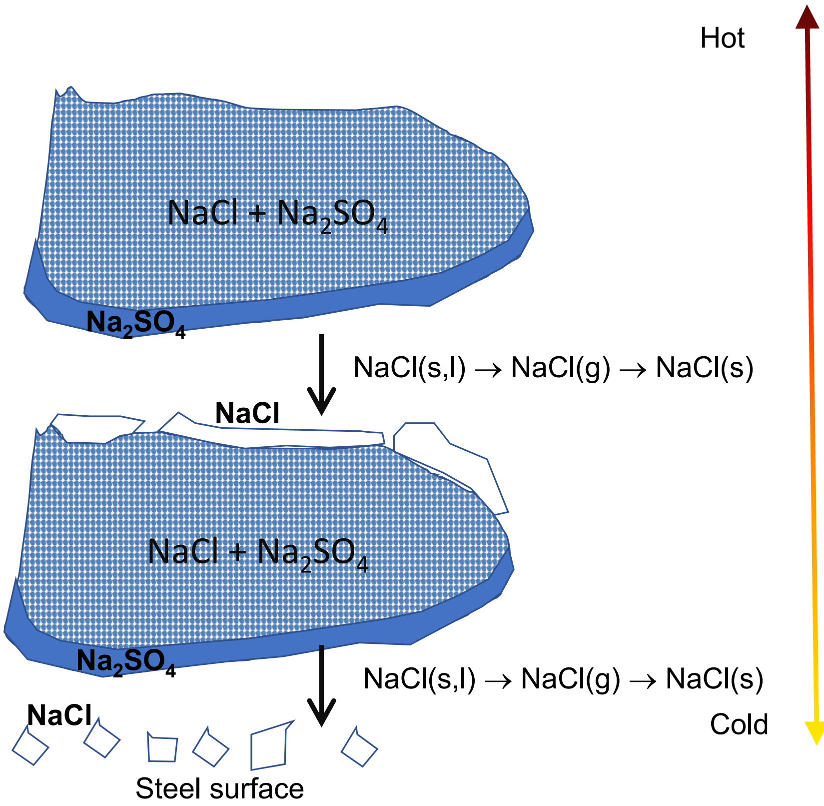
Sulfate/Chloride Deposit in Temperature Gradient



Lindberg, D., Niemi, J., Engblom, M., Yrjas, P., Lauren, T., Hupa, M., Fuel Processing Technology 2016 (14) 285

Salt Grain after 24 h in Temperature Gradient

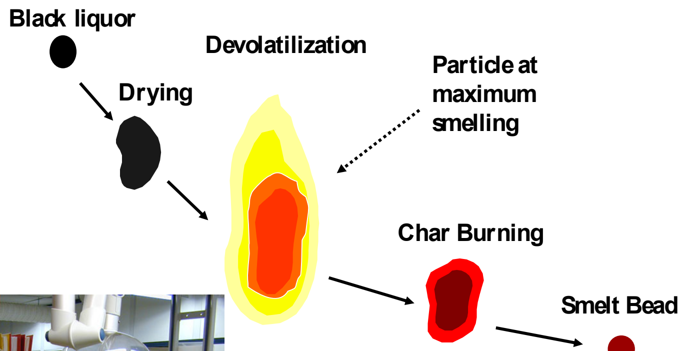


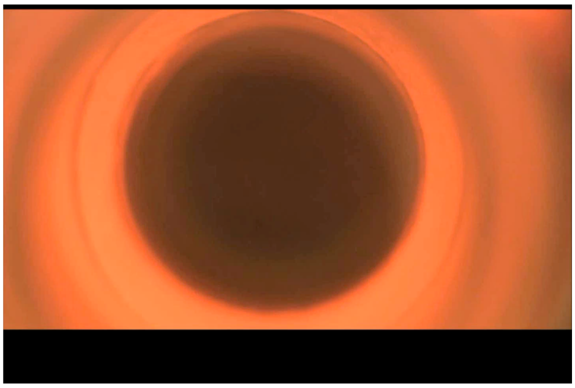


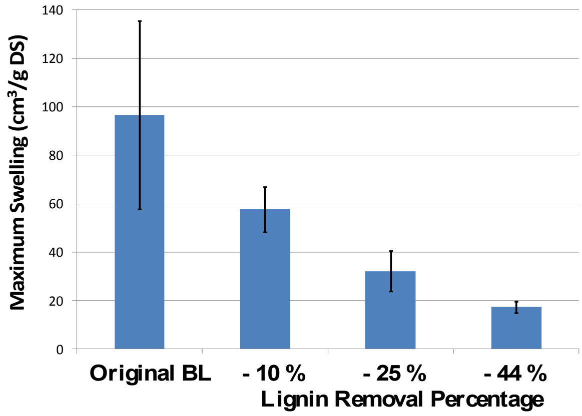
Research Approaches

- Deposit Probes
- Single Droplet Experiments
- Full-scale Measurement Campaigns

Single Droplet Burning Test



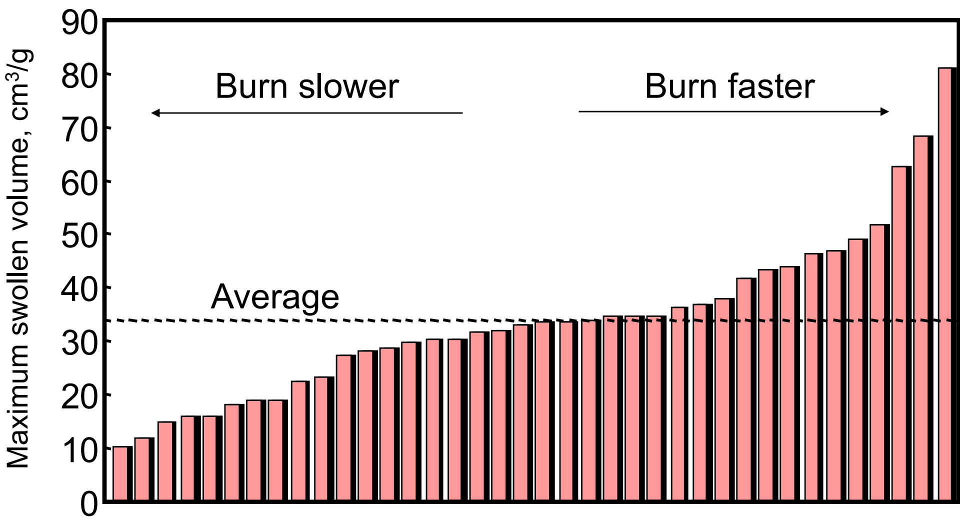




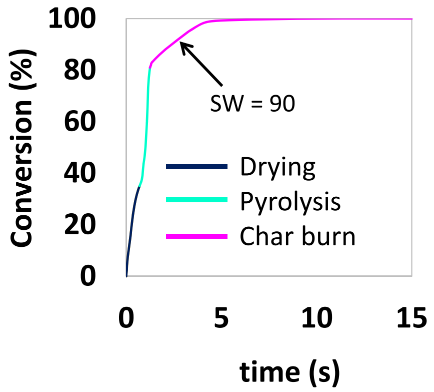
(Hupa et al. 1987, Vähä-Savo et al. 2013)

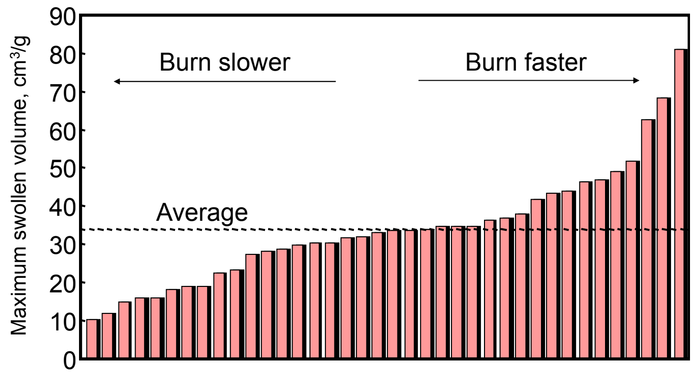
Combustion Swelling for Different Liquors

(500+ Liquors in ÅA Database)

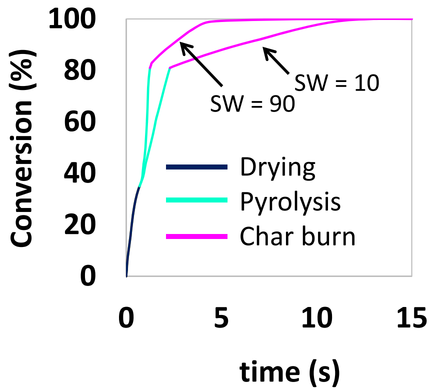


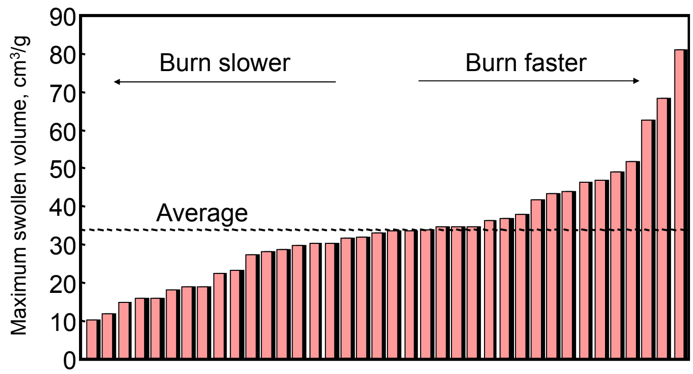
Combustion Swelling for Different Liquors



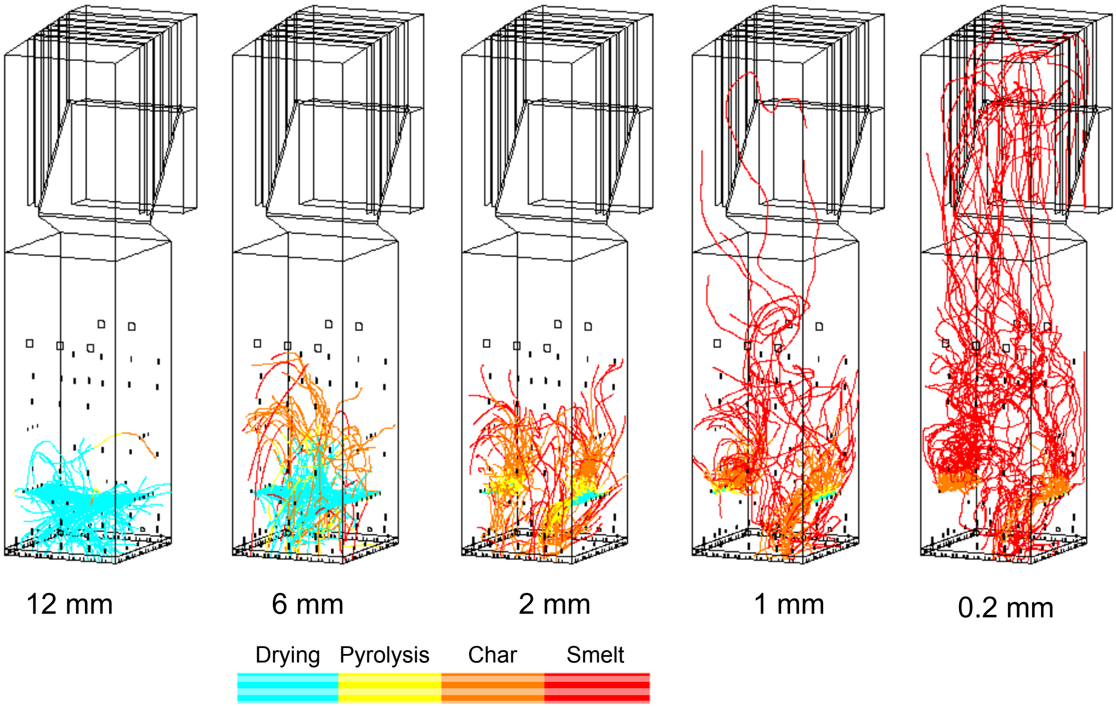


Combustion Swelling for Different Liquors





Trajectories of Liquor Droplets (CFD Results)

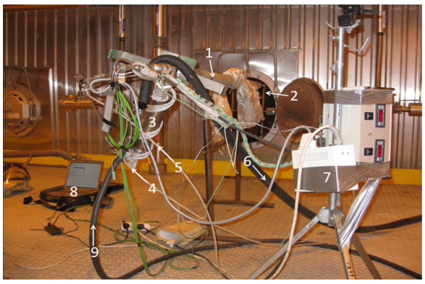


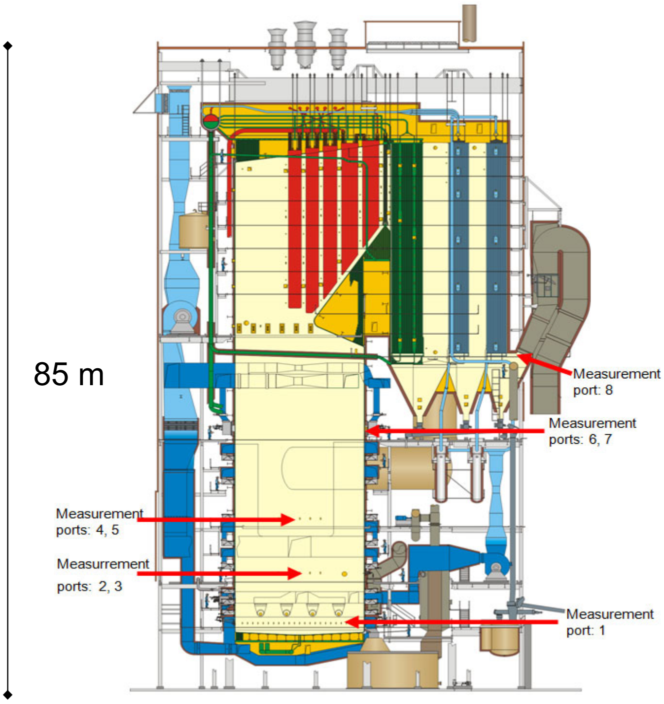
Markus Engblom, Nikolai De Martini, Paulo S.P. da Silva, *CFD-modeling of reduced lignin black liquor combustion*, J-FOR, 7(1), 2018.

Research Approaches

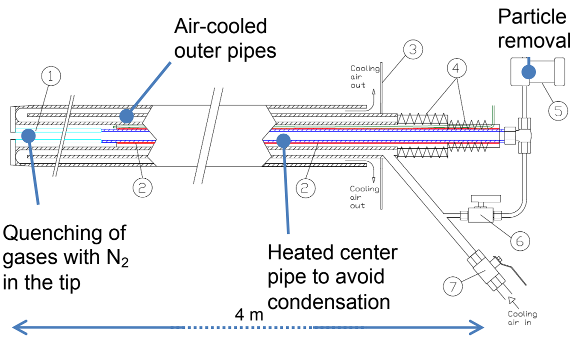
- Deposit Probes
- Single Droplet Experiments
- Full-scale Measurement Campaigns

In Furnace Measurements

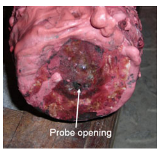


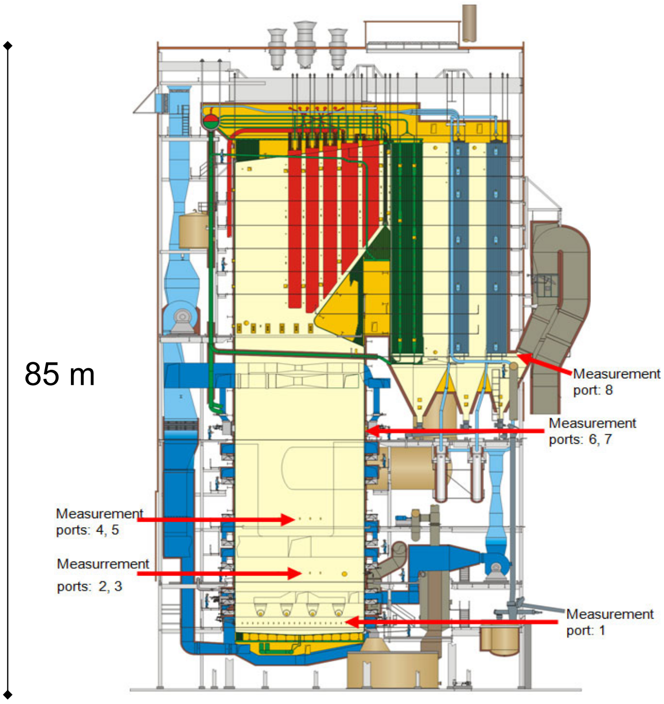


In Furnace Measurements

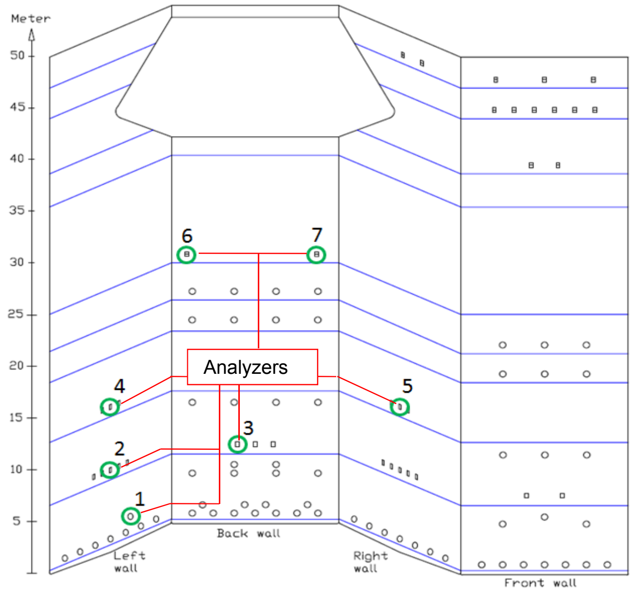


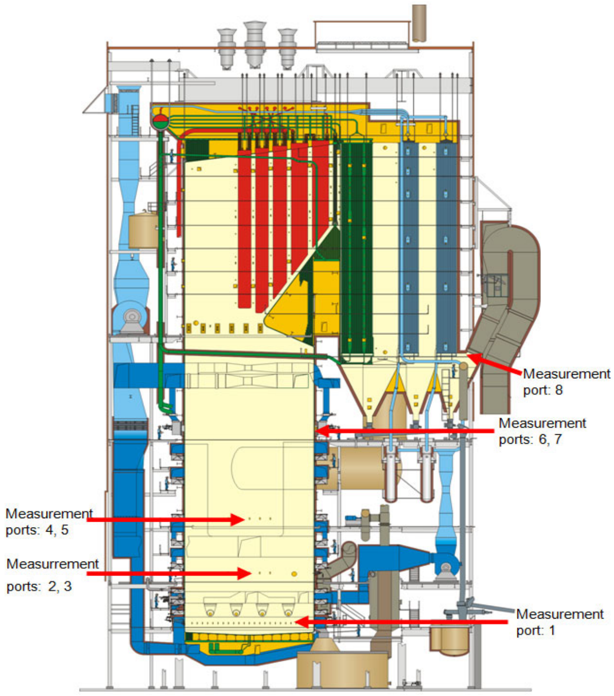
Vainio et al. Energy & Fuels 2012





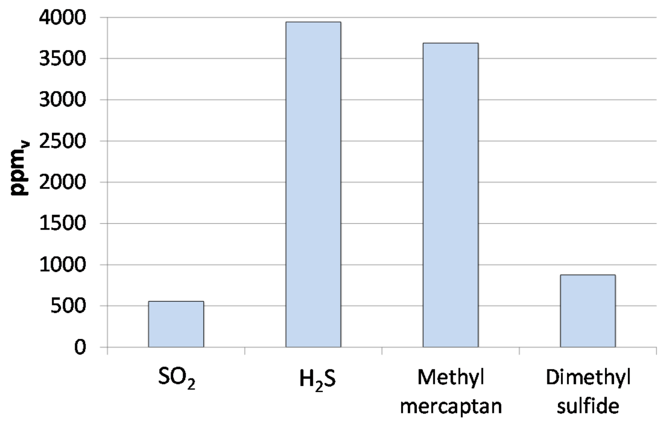
In-Furnace Gas Sampling

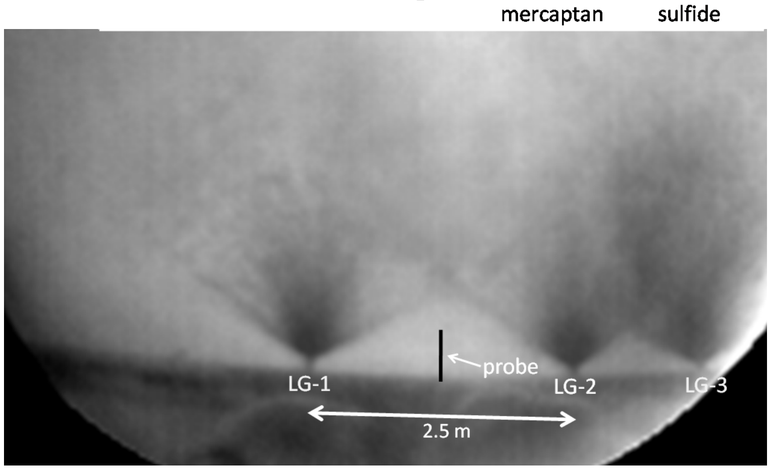


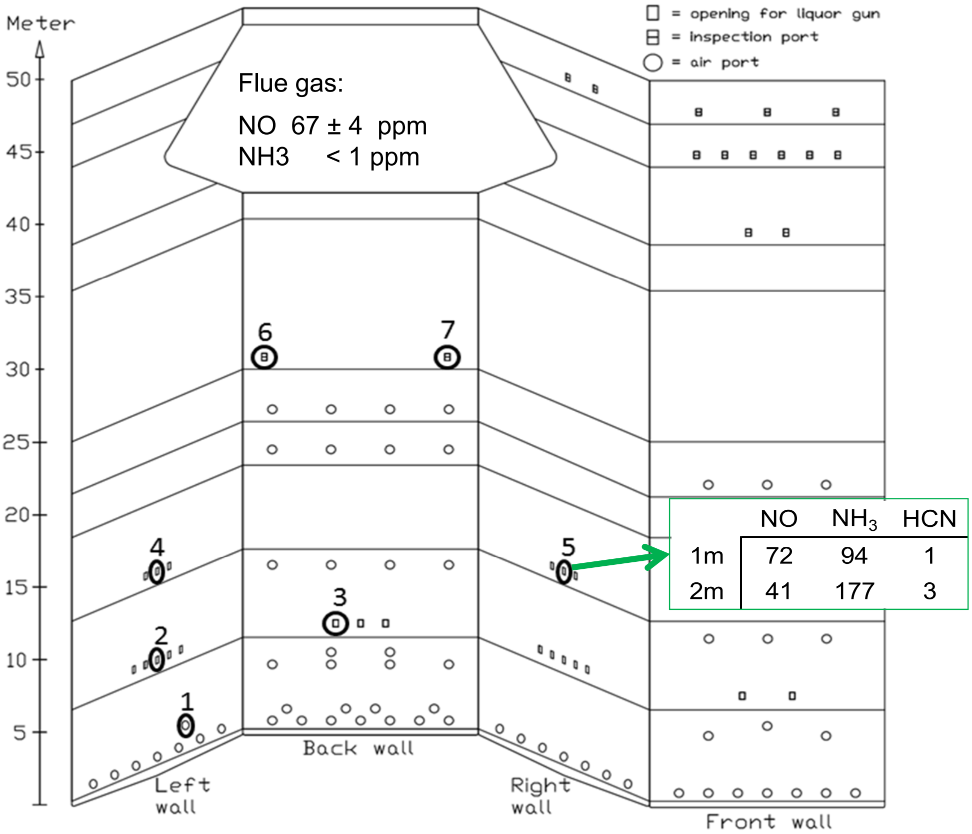


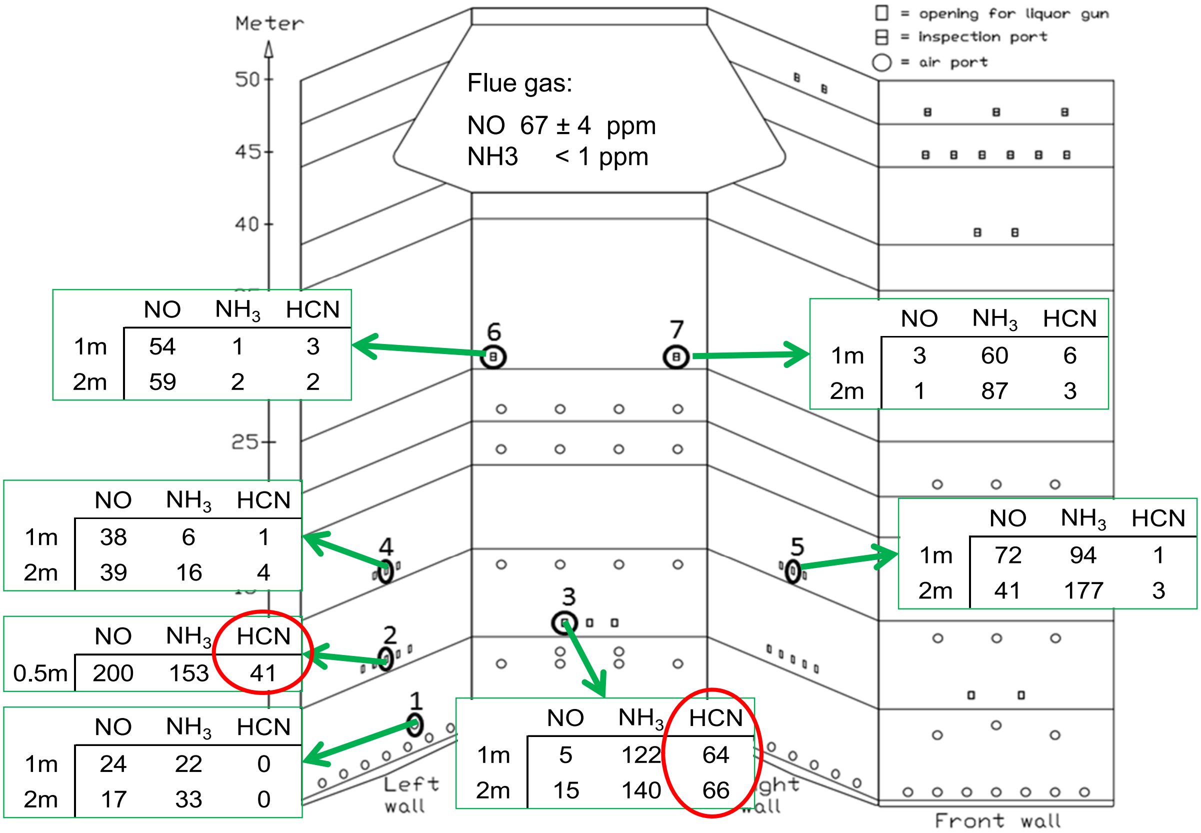
Vainio, E., Brink, A., DeMartini, N., Hupa, M., Vesala, H., Tormonen, K., Kajolinna, T., *Journal of Pulp and Paper Science* 36 (2011)
Engblom, M., Vainio, E., Brink, A., Hupa, M., Välimäki, E., Heikkilä, V-P. *Journal of Science & Technology for Forest Products and Processes,* (2016), 5(6), 24-31.

Sampling between Liquor Guns






Meter
50
45
40
35
30
25
20
15
10
5
□ = opening for liquor gun
⊟ = inspection port
○ = air port
Flue gas:
NO 67 ± 4 ppm
NH3 < 1 ppm
6
7
4
5
3
2
1
NO NH3 HCN
1m 72 94 1
2m 41 177 3
Back wall
Left wall
Right wall
Front wall


Meter
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□ = opening for liquor gun
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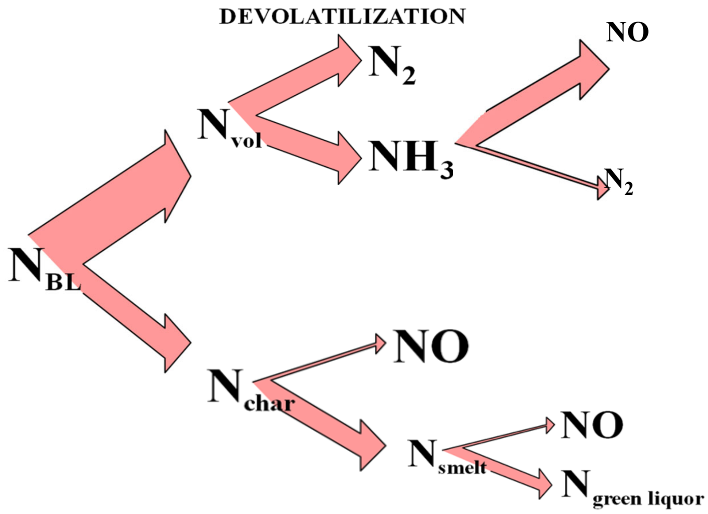
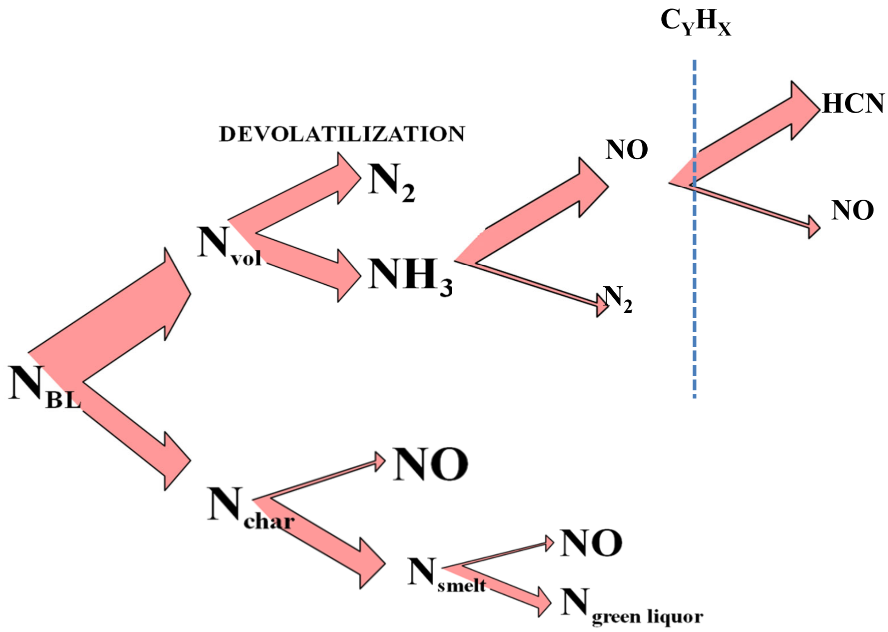
Flue gas:
NO 67 ± 4 ppm
NH3 < 1 ppm
NO NH3 HCN
1m 54 1 3
2m 59 2 2
6
7
NO NH3 HCN
1m 3 60 6
2m 1 87 3
NO NH3 HCN
1m 38 6 1
2m 39 16 4
4
5
NO NH3 HCN
1m 72 94 1
2m 41 177 3
3
NO NH3 HCN
0.5m 200 153 41
2
1
NO NH3 HCN
1m 24 22 0
2m 17 33 0
NO NH3 HCN
1m 5 122 64
2m 15 140 66
Left wall
Front wall

Black Liquor Nitrogen Reactions in Combustion



Forssén, M., Kilpinen, P., Hupa M., NO_x Reduction in Black Liquor Combustion – Reaction Mechanisms Reveal Novel Operational Strategy Options, *TAPPI Journal* 83 (2000)

Black Liquor Nitrogen Reactions in Combustion – Revised



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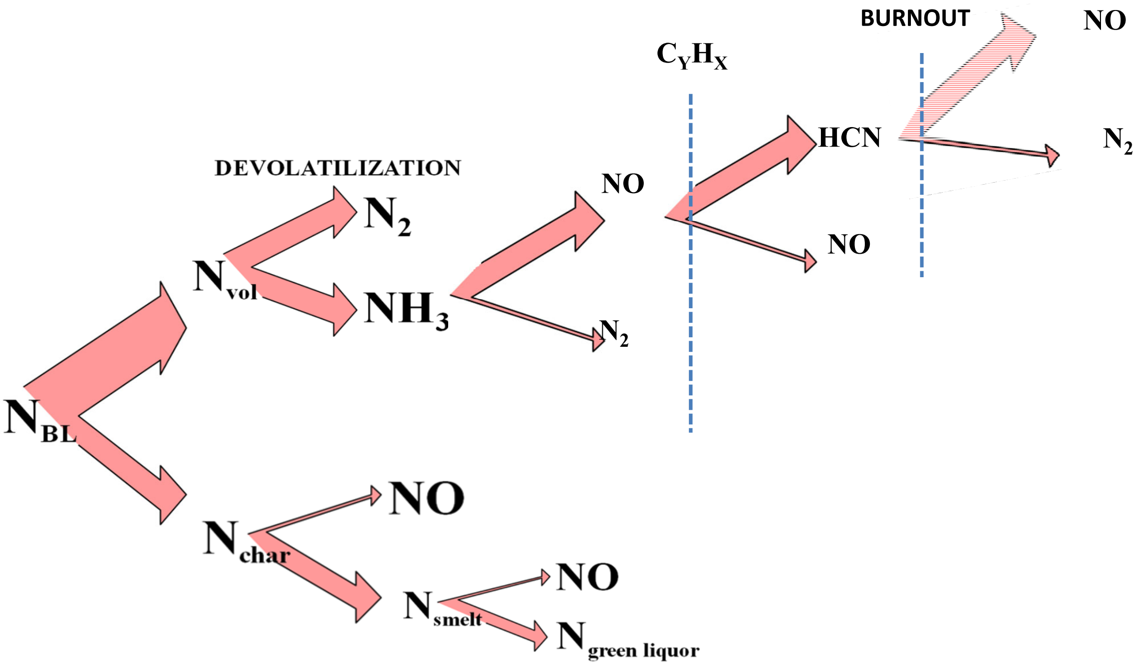
Engblom, M., Vainio, E., Brink, A., Hupa, M., Välimäki, E., Heikkilä, V-P. *Journal of Science & Technology for Forest Products and Processes,* (2016), 5(6), 24-31.

Black Liquor Nitrogen Reactions in Combustion – Revised



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Engblom, M., Vainio, E., Brink, A., Hupa, M., Välimäki, E., Heikkilä, V-P. *Journal of Science & Technology for Forest Products and Processes,* (2016), 5(6), 24-31.

Interrupted Liquor Firing - for Science

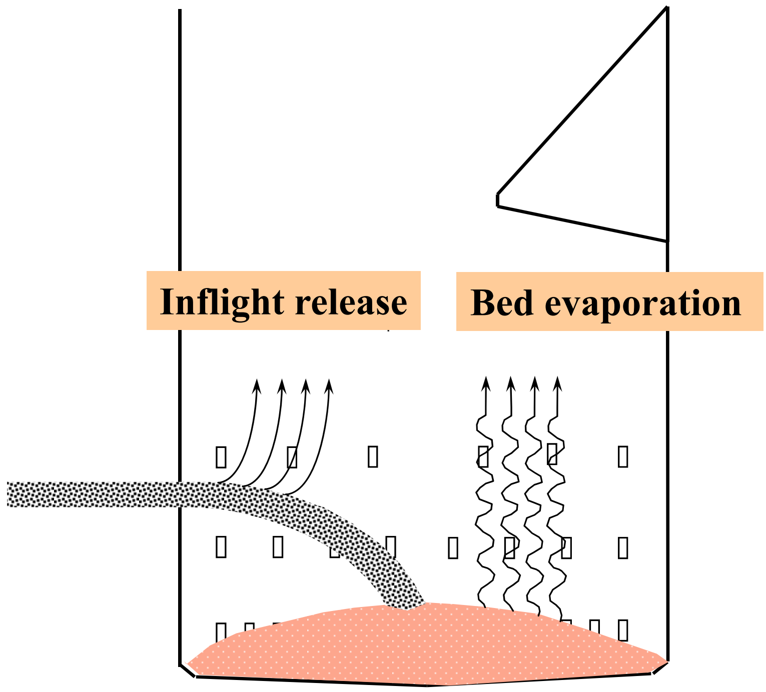
Interrupted Liquor Firing - for Science

Tamminen, T., Kiuru, J., Kiuru, R., Janka, K., Hupa, M.,

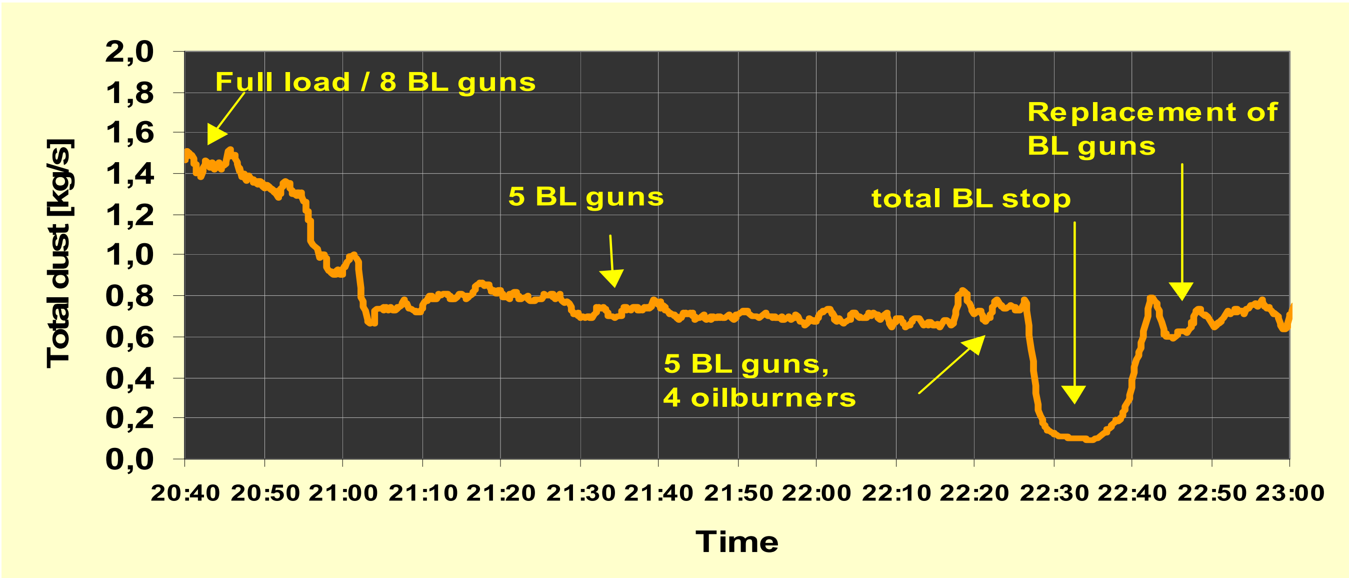
Dust and Flue Gas Chemistry during Rapid Changes in the Operation of Black Liquor Recovery Boilers: Part 1—Dust Formation

TAPPI Journal 85 (2002) 5

Sources of Fume in Recovery Boilers



Dust during Interruption of Liquor Burning – Boiler A



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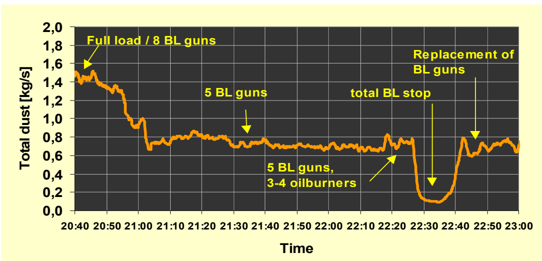

Boiler A

Dust during Interruption of Liquor Burning - Boiler B

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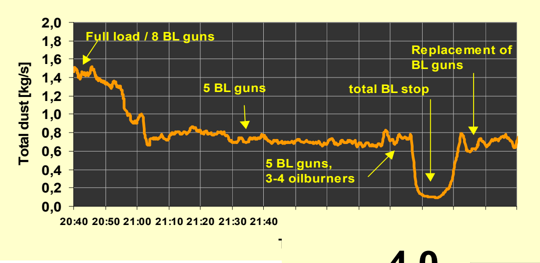
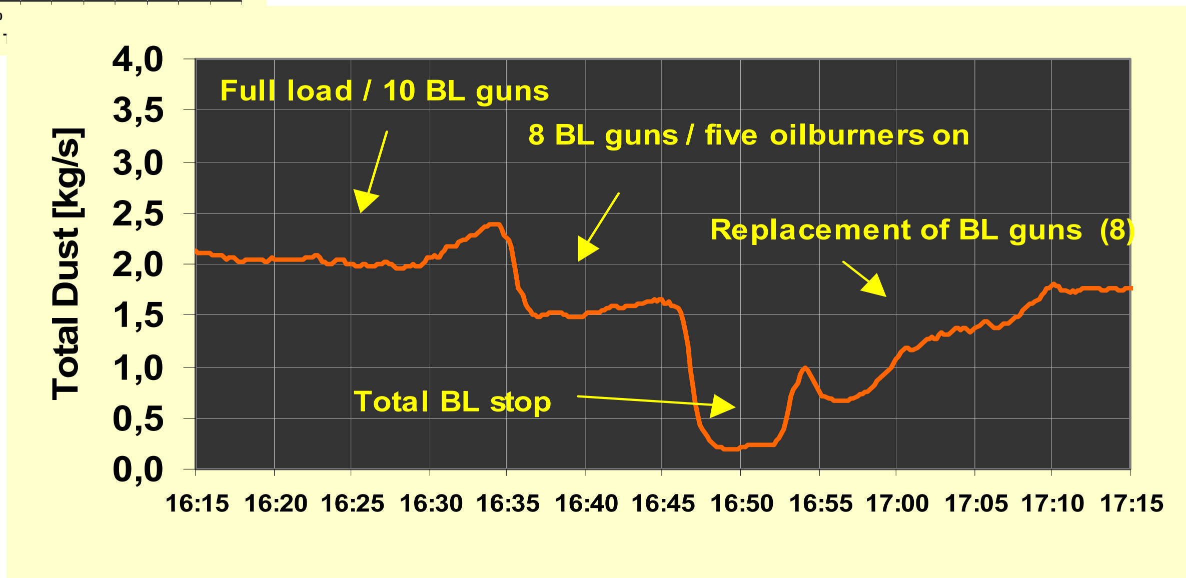


Boiler A



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Furnace Process – Devil in the Chemical Details

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- Understanding of the RB process chemistry dramatically improved
- Finland leading the way

Furnace Process – Devil in the Chemical Details

- Understanding of the RB process chemistry dramatically improved
- Finland leading the way
- Long-term investment in industry-academia research collaboration combining:
  - small scale laboratory studies
  - sampling and measurements in boilers
  - advanced process modelling

Aknowledgements

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FINNISH RECOVERY BOILER COMMITTEE

Research Consortia 2010-2019 ChemCom - FUSEC - CLIFF