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*Samuli Repo*

**Verifying the pulp mill atmospheric emissions from the  
recovery boiler**

Examiners: Professor Esa Vakkilainen  
Professor Risto Soukka

## **ABSTRACT**

Lappeenranta University of Technology  
LUT School of Energy Systems  
Degree Programme in Environmental Technology

Samuli Repo

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Verifying the pulp mills atmospheric emissions from the recovery boiler

2018

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Examiners: Professor Esa Vakkilainen, Professor Risto Soukka

#### **Keywords:**

flue gases, emissions to air, pulp industry, recovery boilers, forest industry, emission balance, emission measurement,

This Master's thesis examines the differences on reported results to calculated air emissions in the real pulp mills. The focus of the study is the difference of reported and modelled flue gas flow for a recovery boiler (RB). The reported results were verified against a created model of combustion and the differences between reported and computed are highlighted. Air emission measurement is a part of monitoring of the RB and is controlled by the authorisation, operator reports the measurement results according the permit states. Usually measurement happens just before the end of the pipe after regulatory air pollution control engineering devices in various locations from the stack and its gas flow. In this thesis is presented the principles of air emission measurement, because reported values are results of measurement of the flue gas from the RB and is a subject matter relative to the thesis. By presenting the more precise flue gas flows of the RB, actions on the pulp mills operation and on air emission reporting are possible. Flue gas amount will be reported at the same oxygen reference level and this should be corrected in the future reports. Flue gas flows averaging and correct value should be presented in the future. Wood species make a big difference to the flue gas amount. Softwood originating black liquor produces more flue gas in RB compared with hardwood originating. Other potential reasons for flue gas amount difference are the yield of pulp, measurement uncertainty, pulp mills processes, boiler overload and by-product capture.

## **TIIVISTELMÄ**

Lappeenrannan Teknillinen Yliopisto  
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### **Diplomityö**

Sellutehtaiden soodakattiloiden ilmapäästöjen tarkistus

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Tässä diplomityössä tutkitaan asioita raportoitujen ilmapäästöjen ja mallinnettujen ilmapäästöjen eroavaisuuksiin sellutehtaissa. Tutkimus keskittyy soodakattilan savukaasumäärään – raportoituun ja mallinnettuun. Vertaillaan tehtaan päästömittauksien perusteella raportoimia tuloksia ja tehtyjen tehtaan massataseen laskennan avulla saatuja arvoja. Päästömittaus on osana sellutehtaiden soodakattilan valvontaa ja sitä ohjataan lupamenettelyllä, toiminnan harjoittaja raportoi luvanmukaisesti päästömittauksen tulokset. Yleensä päästömittaus tapahtuu juuri ennen piipun päätä savukaasupesurien ja -suodattimien jälkeen sen sisällä virtaavasta savukaasusta. Työssä esitetään päästömittauksen peruseriaatteet, koska raportoidut arvot ovat saatu mittaamalla savukaasua ja on yksi aihealueesta työn kannalta. Esittämällä sellutehtaiden soodakattiloiden savukaasuvirtauksia tarkemmin, voidaan vaikuttamaan tehtaiden toimintaan ja ilmapäästöjen raportointiin tulevaisuudessa. Savukaasunmäärä tulee raportoida samassa määrättyssä happipitoisuudessa ja keskiarvoistus sekä määrän ilmoittaminen tulee tehdä oikein tulevissa raportoinneissa. Puulajilla on vaikutusta savukaasumäärään. Havupuista peräisin oleva musta lipeä tuottaa enemmän savukaasua soodakattilassa verrattuna lehtipuista peräisin olevaan. Muita potentiaalisia syitä savukaasumäärän eroavaisuuksiin ovat saanto, mittauserätarkkuus, sellutehtaan prosessit, kattilan ylikuormitus ja sivutuotteiden talteenotto.

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Appendix I Mill B typical information given in datasheet for measurement of recovery boiler

Appendix II Example of model of combustion, model for the Mill G

Appendix III Emissions to air EU specific standards periodic and continuous

## LIST OF SYMBOLS

ADt	air dry tonne
APC	air pollution control
AMS	automatic measuring system
BREF	best available techniques reference document
CEMS	continuous emissions monitoring system
CEPI	Confederation of European Paper Industries
CHP	combined heat and power
CNCG	concentrated non-condensable gas
DNCG	diluted non-condensable gas
EMAS	Eco-Management and Audit Scheme
N	normal state and standard state in this document 273 K, 101,3 kPa
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzodioxins
PCDF	Polychlorinated dibenzofurans
PM	particulate mater
PP	pulp and paper
RB	recovery boiler
TRS	total reduced sulphur

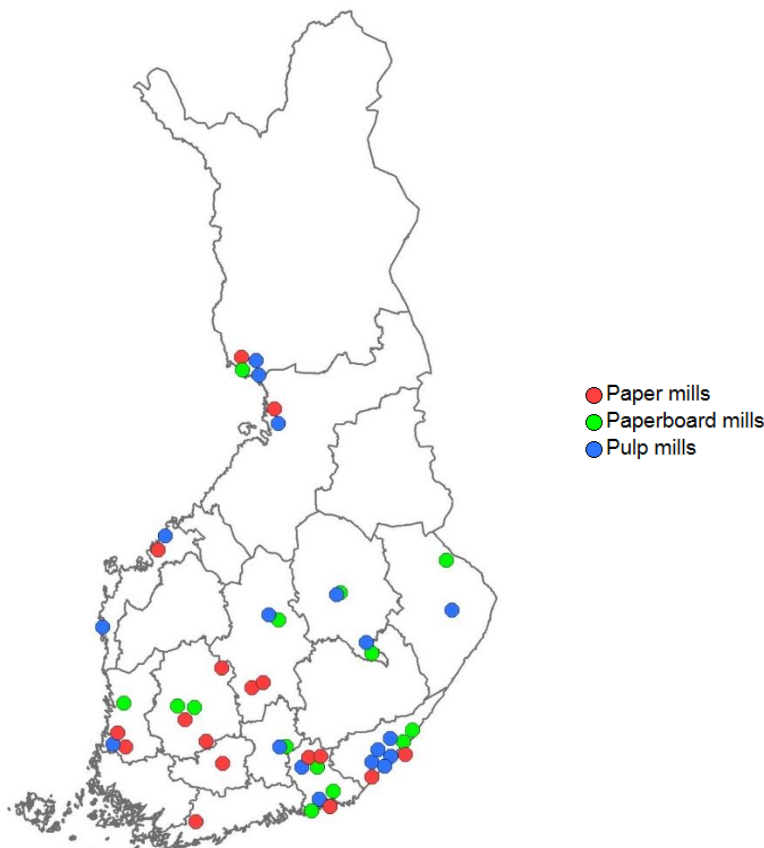
# 1 INTRODUCTION

## 1.1 Background

Kraft pulp mills are common method for producing cellulose fibre out of wood-based materials. Recovery boiler (RB) burns uncaptured wood-based materials, mainly containing lignin. Efficient use of burning of masses reduces amount of CO, NO<sub>x</sub> and sulphur emissions (Knowpulp 2018; Dahl 2008, 16). Flue gases contain mainly combustion products and air (N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>), but in minor concentration suspended materials, sulphur dioxide, hydrogen sulphur, carbon monoxide and oxides of nitrogen (Knowpulp 2010). Nitrogen oxide chemistry in incineration processes is harder to model or simulate. Nitrogen oxides are mainly forming from the N-molecules in the fuel. Suspended solids or ash from boiler consists mainly of Na<sub>2</sub>SO<sub>4</sub>. Emissions need to be reduced, because emissions from industry or power plants can cause health risks and environmental destruction (Peavy et al.1985, 417–480). Clean production costs in building phase are investments in the technological appliance, but reductions of costs due to pollution risks in the future may be avoided by making these appliances available in the power plant.

Modern day pulp mills have to report their emissions. Mainly total emissions depend on the production rate of pulp, specific emissions are reported along overall emissions. There are standards that are followed in whole EU countries, so we have equivalent measurement techniques for measurements compounds (emission control and measurement is common in EU countries, every country has its own responsibilities to implementation). Standards are being followed in emission measurement, depending where and what type of plant is in operation. Standardized measurement techniques are presented in these standards ( Appendix III). Modelling of flue gas volumetric amounts to produced ton of pulp is done from energy balance or measurement data. Still industry uses combustion models, calculations, rather than continuous flow metering of the flue gases in the stack of the RB (EIPPCB. 2008). Professional expert comments that continuous flow measurement is now prevalent.

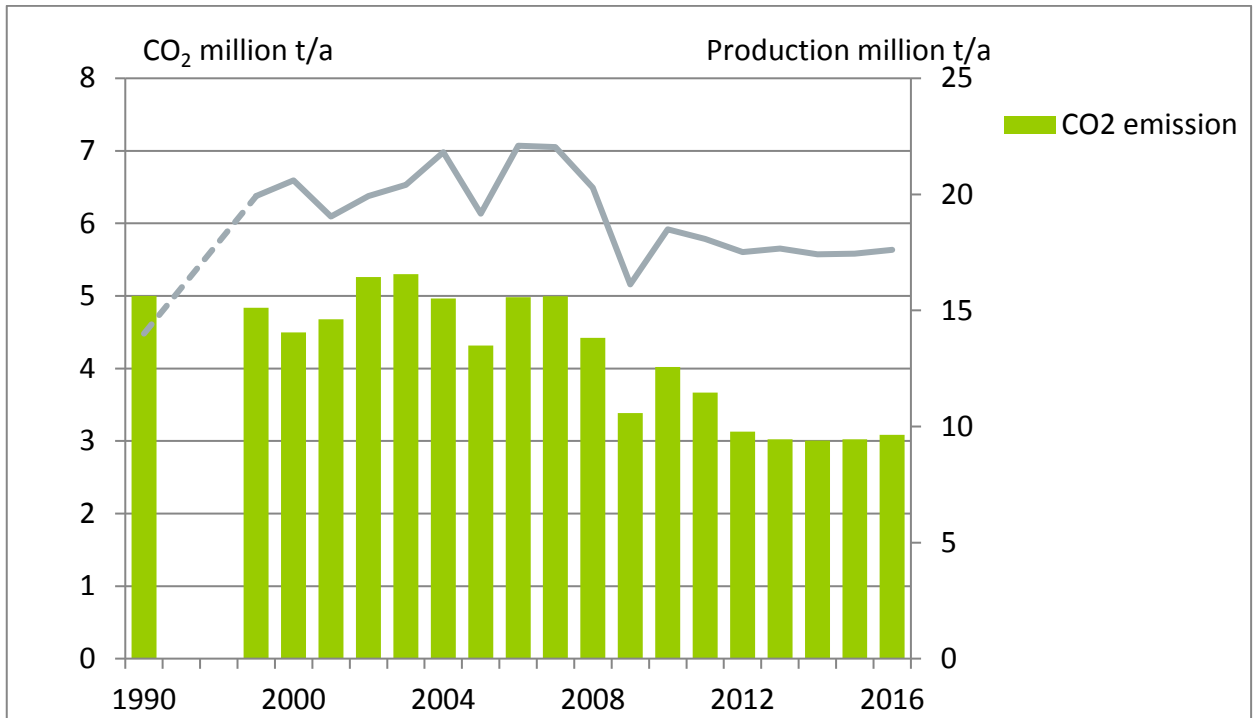
Discussion on other use of black liquors content, especially lignin, is the research topic of many reports and articles. Lignin is still mainly burned for making of electricity and heat. Steam is used in industrial processes. Emissions from the chemical pulp mills were reduced significantly during the past years. In 15 year period 70 – 80 % is been reduced (Knowpulp 2010). Figure 1 presents the current paper mills, paperboard mills and pulp mills in Finland in year 2017.



**Figure 1** Finnish paper-, paperboard- and chemical pulp mills that are in operation in 2017 (Finnish Forest Industries 2017).

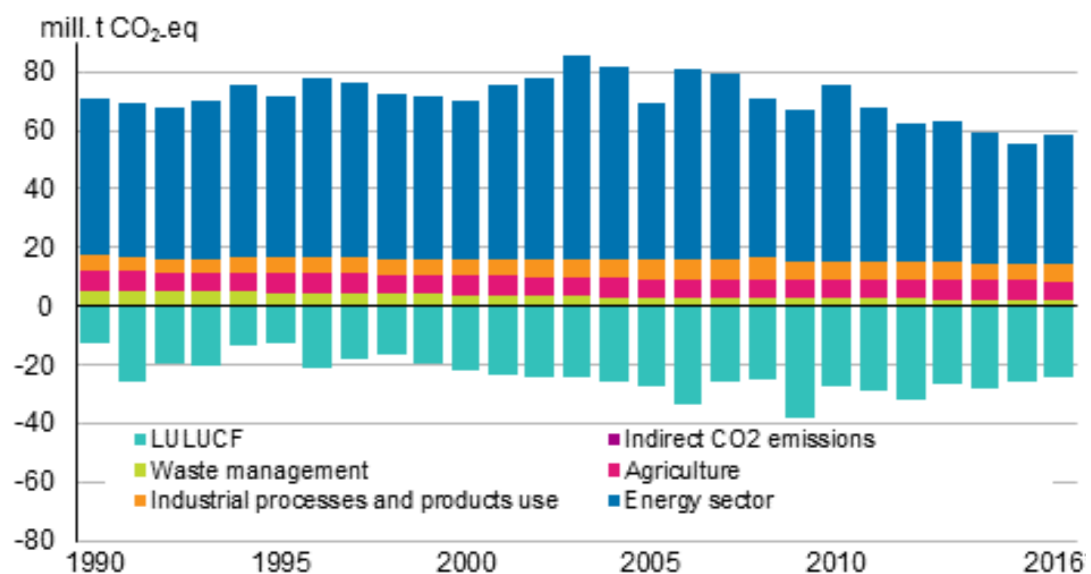
CO<sub>2</sub> emissions are calculated from fossil fuel emissions only. Figure 2 represents those fossil emissions that are due to pulp and paper industry. Land use change and forestry sector (LULUCF) is negative in Finland, forest engineering and sustainable forest management captures carbon from the atmosphere and it is known that denser forest cover cleans air from other pollution such as particles, sulphur, nitrogen oxides and other combustion-sourced emissions. Thanks to forest industry it is economically viable to take care of forestry in right manner that growing stock is increasing faster than felling. CO<sub>2</sub>-emissions due to LULUCF should be carefully observed and monitored.





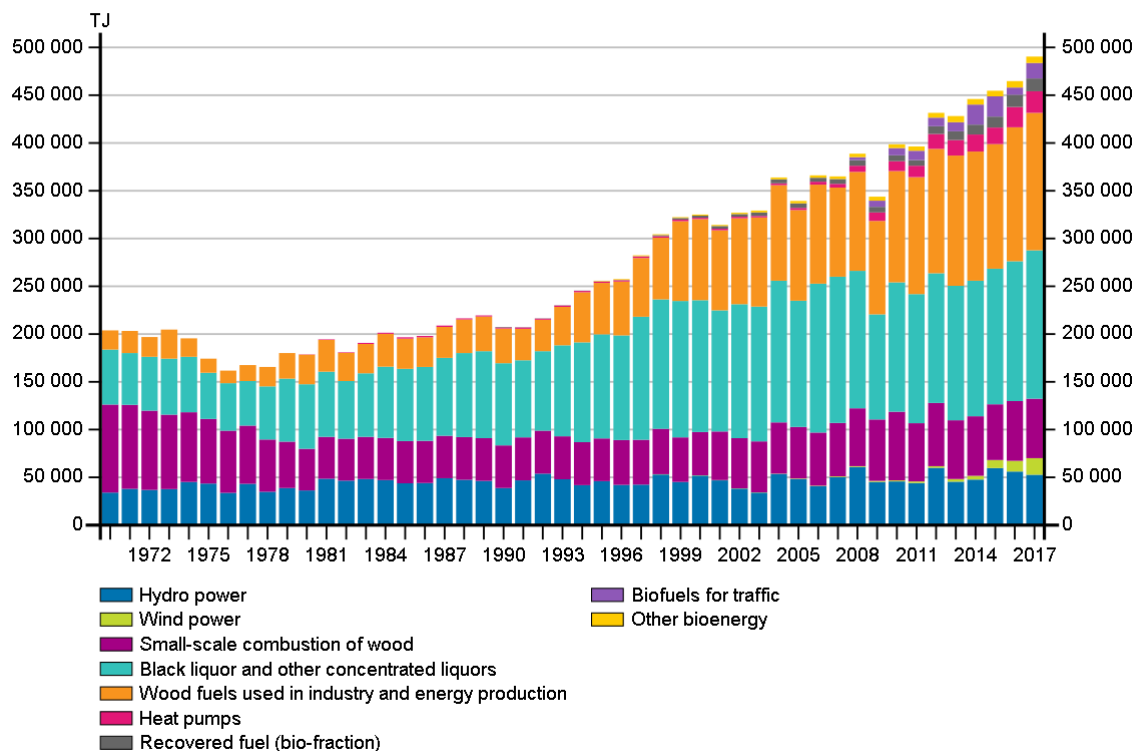
**Figure 2** Fossil CO<sub>2</sub> emissions from the pulp and paper industry in Finland (Finnish Forest Industries 2017)

The latest estimate is from the year 2016 in Figure 2 9,8 million tons of CO<sub>2</sub> fossil emissions from the pulp and paper industry. Greenhouse gas (GHG) emissions in Finland are presented in Figure 3. LULUCF is a removal when all the operations are calculated together. Operations in LULUCF include forestland, harvested wood products, settlements, grassland, cropland and wet lands (Statistics Finland 2017).



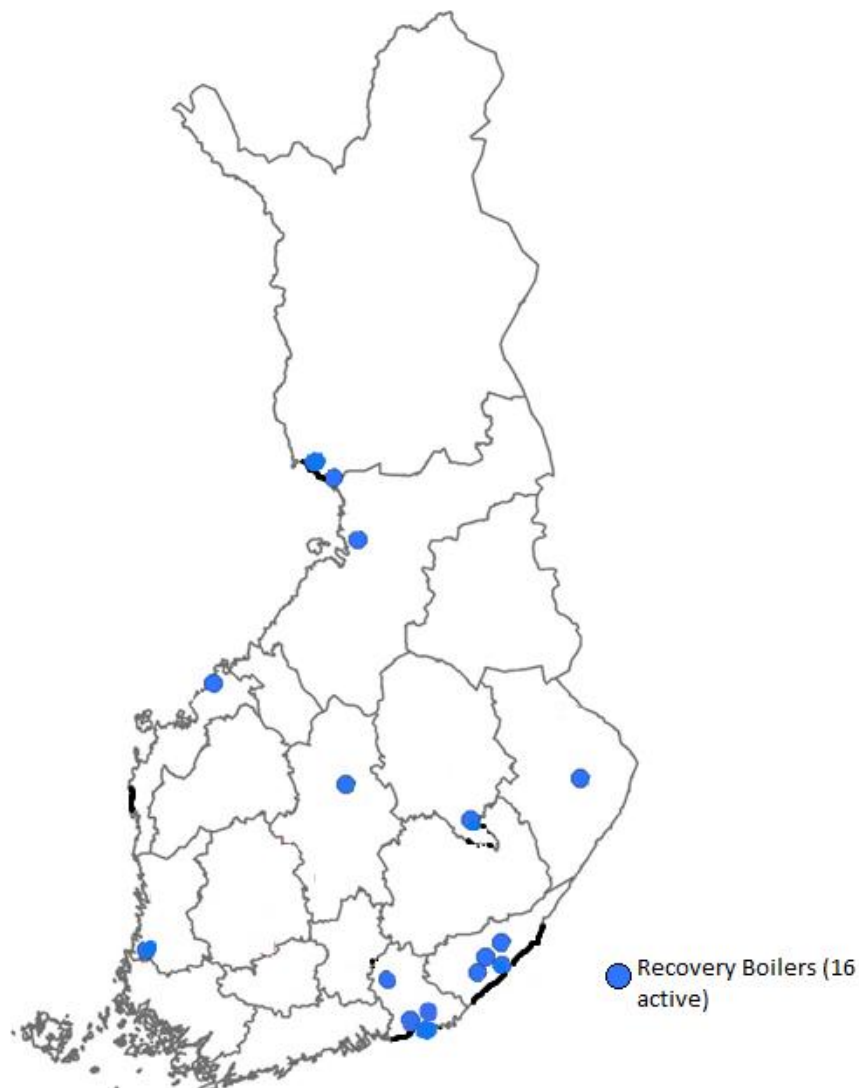
**Figure 3** Sectors and their amount of GHG emissions in Finland from year 1990 to 2016 (Statistics Finland 2017)

Environmental awareness in Finnish pulp mills and energy efficiency has resulted in increasing the values of companies – better operation results in more pulp to the market. This implies more sale and expenditures per produced ton of pulp or bio-based materials becomes lower. Over the years, focusing on environmental technology improvements have contributed great savings in the mills operation and has been beneficial to the environmental protection and resource efficiency. To generalize pulp mills goal is to increase production levels without placing further strain on the environment. Modern forest industry seems to be interested in researching and finding new technologies to utilize lignin, the main organic component in black liquor to be combusted in RB. Piloting products on refining lignin for plastics or carbon fibre is attractive. Nanocellulose is one newest research emerging and other example of emerging technologies in bioeconomy is clothing suitable fibre made from the wood. In Figure 4 presented renewable energies, the share of renewable sources in energy production has steadily increased during last decades in Finland. Some future changes might be in situ if black liquor utilization will be partly shifted to the separated lignin.



**Figure 4** Consumption of renewable energy sources in Finland (Findicator 2017.)

In Finland year 2008 there were 15 kraft recovery boilers with startup time from 1965 to 2008 and the median startup year 1989. Renewable based products need energy – heat in the form of steam and electricity to be manufactured. Boilers main function is to generate these. Black liquor is still the most significant fuel of bioeconomy, it is a biomass fuel. Bark combustion boiler is a one other type of biomass boiler. (Statistics Finland 2017)



**Figure 5** RBs active in Finland 2018 – there are 16 of them operating. Sunila mill and Imatra mills have two RBs in operation.

## 1.2 Objectives and scope

There has been more and more attention towards RBs flue gas emissions and monitoring in recent years (Aumala 2000, 323; Wessman 2007, 5–8; Pinkerton 2014, 9). Technologies in use apply; best available techniques in EU are to be utilized. Information from several mills is reported via different channels such as EMAS, sustainability reports and Finnish forest industries statistics. The main environmental performance document and guideline in the EU is BAT BREF Best Available Techniques (BAT) Reference Document for the Production of Pulp, Paper and Board, which explains this branch of industries best practices. BREF will be revised after certain periods by the authorities, this thesis work uses 2015 version of the BREF.

This Master's thesis looks at statistics and models kraft boilers flue gas amounts in respect to wood species in Finland for every RB containing pulp mill. Wood species are mainly birch and pine. Flue gas amount is determined from fuel analysis (C,H,O,N,S, ash, moisture and energy content are analysed and used as data input to mathematical modelling which involves flow calculation). Reported flue gas flows were collected from most of the pulp mills in EU in year 2008. Off-gas volume represents the amount of combusted mass to gases that exit stack flue. Verifying the amount of combustion gas flow is important as verifying of amount of pollutant depends from it. Certifying flue gas flow rate in respect to produced pulp is important for the future reports, because modelled and reported values differ currently, also oxygen content of the flue gases was seemingly not uniformly reported in 2008. Statistics offer also the year 2016 mill specific air pollutant emissions and pulp production rates, where it is researched NO<sub>x</sub> emissions to the years 2016 balance.

## **2 WOOD SPECIES AND COMPOSITION**

Wood species are many in forest-covered countries. This chapter only examines the wood species that are possible to use in chemical pulp in the industry of Finland and are grown in Nordic forests. There are some main wood species found and used by forest industries. General division in wood species to two categories are hardwood and softwood. In statistics are usually written spruce, pine and softwoods.

Wood is a three-dimensional biopolymer composite composed of interconnected networks of cellulose, hemicellulose and lignin and minor amounts of extractives and inorganics. Naturally, the main component of a living tree is water. Dry-weight basis wood cell walls consist mainly of sugar-based polymers carbohydrates that are combined with the lignin. Elemental composition of dry wood has 50 % carbon, 6% hydrogen, 44% oxygen and trace amounts of inorganics. (Rowell et al. 2005, 36)

Section 2.1 will be some specific data given from wood species and their composition. Subsection 2.1.1 has some pictures of wood cells and the construction of wood. Subsection 2.1.2 pulp mills wood consumption is presented.

### **2.1 Wood species**

We have many wood species in paper and pulp industry to be feed to the pulp mill and even more in the whole forest industry including sawmills, furniture– and joinery industry. Usage of different wood species is important for obtaining desirable product. Territorially there are significant differences on which wood species are growing for lodging. Zone of supply is limited for environmental and economic reasons, too long driving distances one reason.

Table 1 presents all the domestic grown and utilized wood species in pulp industry in Finland.

**Table 1** Common wood species in Finnish forests that are used as raw material in kraft pulp mills

pine, scots pine	<i>Pinus Sylvestris</i>
spruce, norway spruce	<i>Picea abies</i>
birch, silver birch, downy birch	<i>Betula pubescens</i> and <i>Betula verrucosa</i>
aspen	<i>Populus tremula</i> , <i>Populos tremuloides</i> and <i>Populus tremula</i> × <i>tremuloides</i> Michx
alder, grey alder, black alder	<i>Almus incana</i> , <i>Almus glutinosa</i>

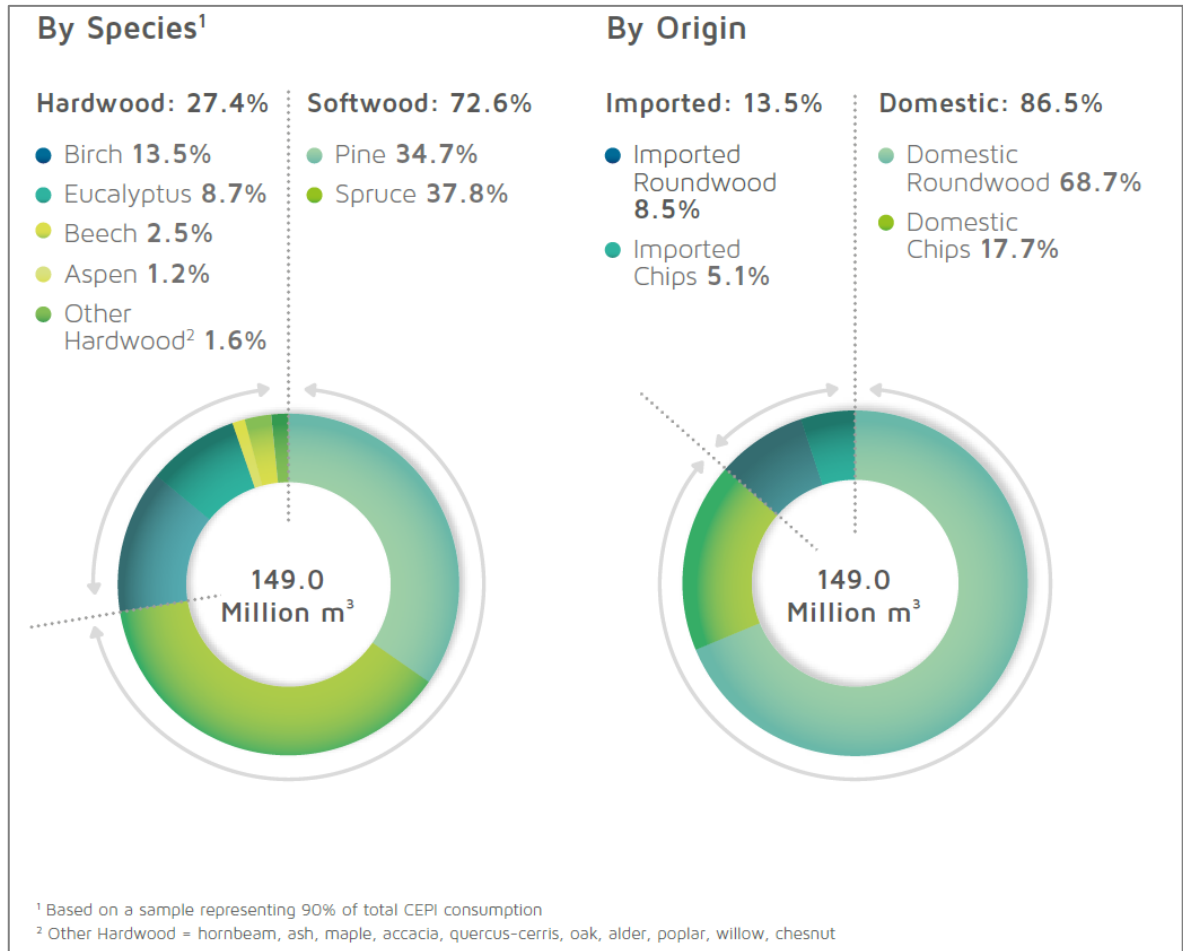
From table 1 presented species pine, spruce and birch are the main three by total mass. In table 2 is presented the main trees chemical composition.

**Table 2** Chemical composition of wood species [m-%] (Henriksson et al.2009, 24)

<i>Species</i>	<i>Extractives</i>	<i>Lignin</i>	<i>Cellulose</i>	<i>Glucomannan</i>	<i>Xylan</i>	<i>Other polysacch.</i>	<i>others</i>
<i>Norway Spruce</i>	1,7	27,4	41,7	16,3	8,6	3,4	0,9
<i>Scots Pine</i>	3,5	27,7	40,0	16,0	8,9	3,6	0,3
<i>Birch</i>	3,2	22,0	41,0	2,3	27,5	2,6	1,4

Birch has lower lignin content than softwoods. Figure 6 presents CEPI collected data in year 2017 in CEPI countries.

In EU pine, spruce and birch account 86% of total wood species consumed in pulp and paper industry. CEPI countries are EU countries plus Norway. CEPI includes pulp, paper and board.

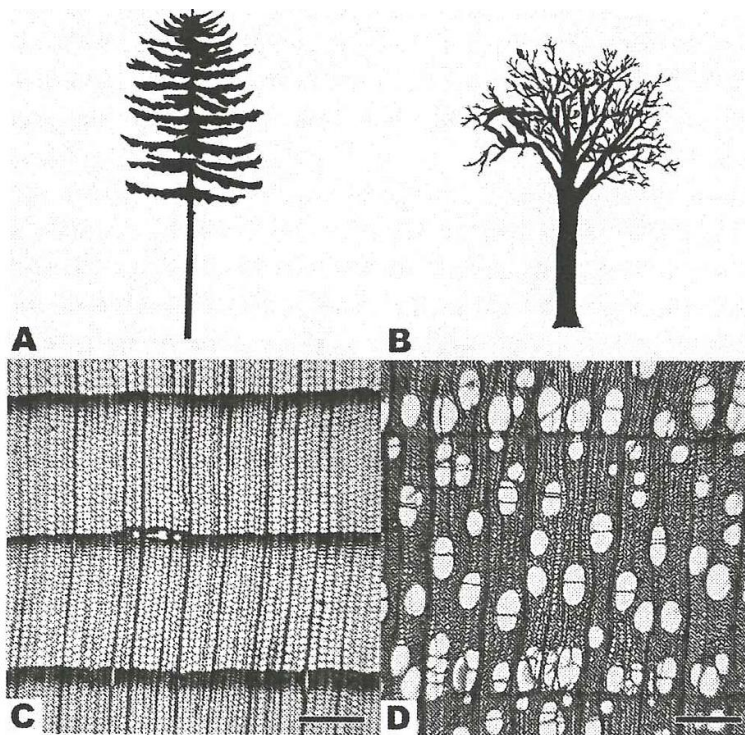


**Figure 6** Main species consumed in CEPI countries in year 2017 (CEPI, 2017)

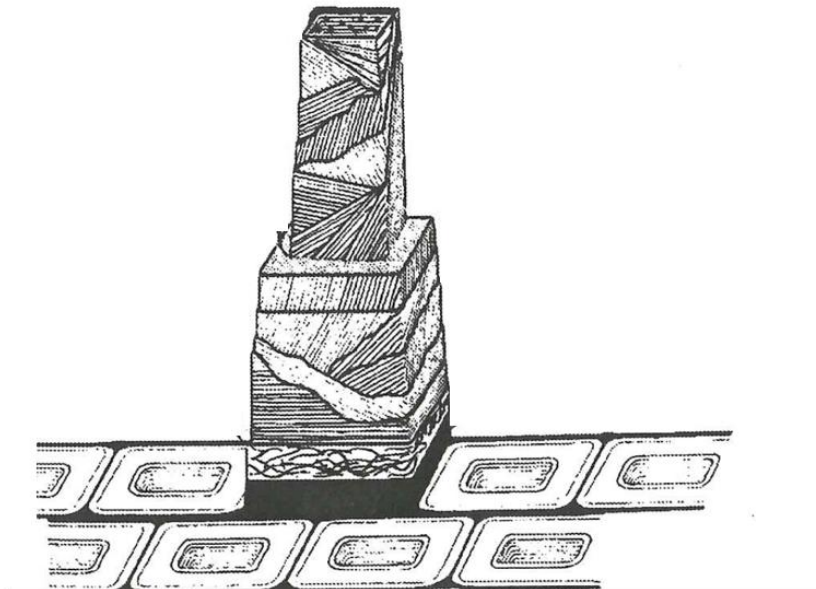
Literature offers large data of many main wood species and their average content. All the continents have history of different species used in industries and new raw materials are under research, for example non-wood/by-product materials for instance Malaysian oil palm empty fruit punches. Included in this thesis are most significant data in the matter of thesis.

### 2.1.1 Pictures of wood cells and construction

Figure 7, presented differences between typical softwood and hardwood, not only chemical composition is different, but also outlook in growing stage and in the microscopic image is different between hardwood versus softwood. Structure of hard wood and softwood is different at the cell level. In Figure 8 is shown scots pine cell wall; a schematic picture. Soft woods mostly contain tracheid (Jääskeläinen&Sundqvist 2007, 36). Other wood cells in softwood are ray parenchyma cells and epithelial parenchymatous cell.



**Figure 7** A softwood configuration B hardwood configuration C Douglas firs transverse section, typical softwood D transverse section of yellow birch a typical hardwood. Scale bar in C and D is 300  $\mu\text{m}$ . (Wiedenhoeft 2005, 11)

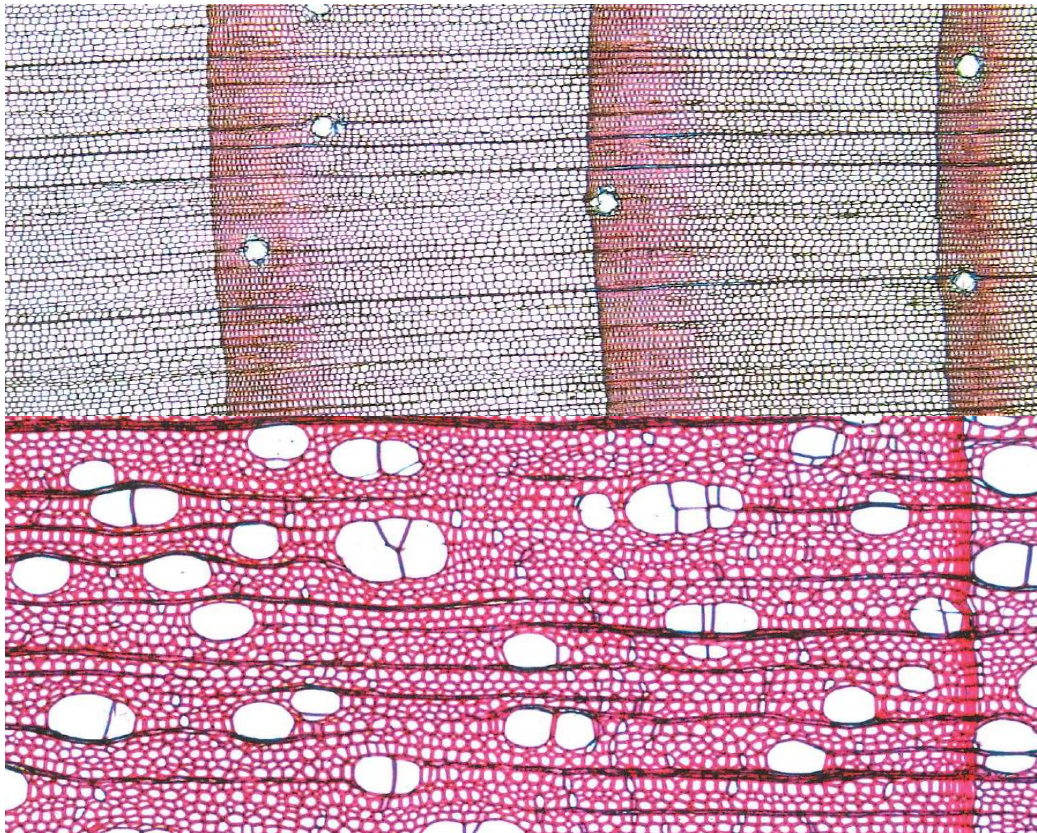


**Figure 8** Schematic picture of cell wall of the scots pine (Rowell et al. 2005, 51)



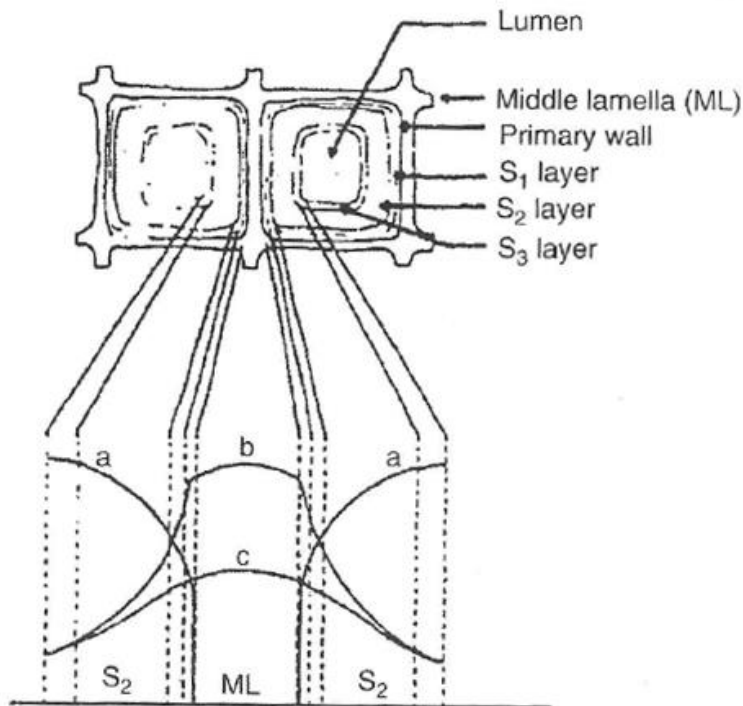
Softwoods have resin canals. Around those canals are epithelial cells (Jääskeläinen&Sundqvist 2007, 41). Juniper tree does not have resin canals, but pine and spruce have resin canals, all softwoods contain some amount of resin and extractives, while parenchymatous cells contain those both (Jääskeläinen&Sundqvist 2007, 41). Wood cell wall chemical constituents vary in depending on part of the cell wall. Genetics make plants grow a certain way and interact with the environment, drawing to its parts different chemicals more than other in proportions for growth. Trees are living organic matter and they have some minor inorganic content, specially tropical and subtropical trees may contain more inorganics up to 5% mass content (Jääskeläinen&Sundqvist 2007, 105).

Hardwoods have leaf drop annually. Leaf drop needs efficient fluid and nutrient transference. There are more kinds of wood cells in hardwoods than softwoods. Hardwoods have fibers, tracheid, vessel elements and parenchymatous cells. Vessel elements move water effectively radially in hardwoods. (Jääskeläinen&Sundqvist 2007, 41–46)



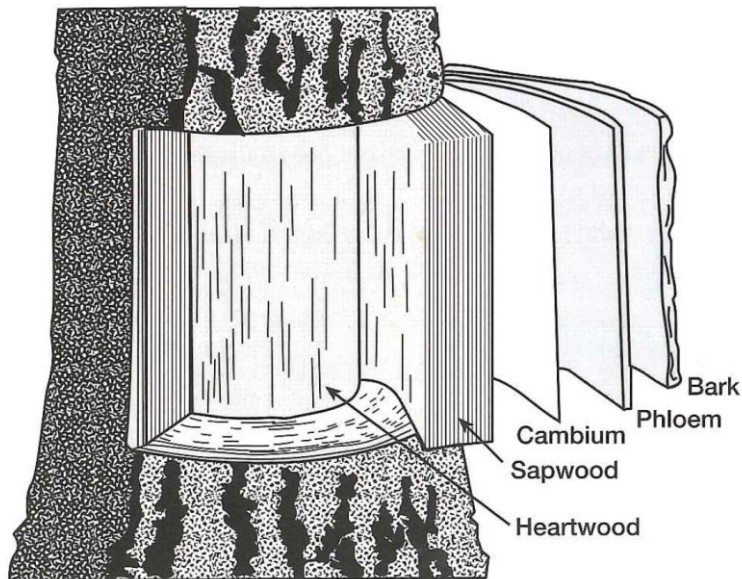
**Figure 9** Upper crosscut is pine, down crosscut is birch. Birch has main part is fibre. Pine has those resin canals white holes, difference is macroscopic between these two species (Kärkkäinen 2007, 39, 49). Photos by Pekka Saranpää.

Larger part of the lignin is in cell walls and majority of cellulose exist in inner cell. This is demonstrated in figure 10. Layers are in the following order from inside to outside lumen,  $S_3$ ,  $S_2$ ,  $S_1$ , primary wall and middle lamella. Middle lamella has the highest content of lignin.



**Figure 10** Wood cell has relative amounts of a) cellulose b) lignin c) hemicellulose Lumen, Middle lamella primary wall,  $S_1$  layer  $S_2$  layer and  $S_3$  layer are typical in literature presented wood cell division. (Williams. 2005, 148)

Pulp is in the cellulose, which is at its highest in the  $S_2$  layer. For knowledge of some general parts of the wood, terms used to defined wood bark, wood trunk is in figure 11.

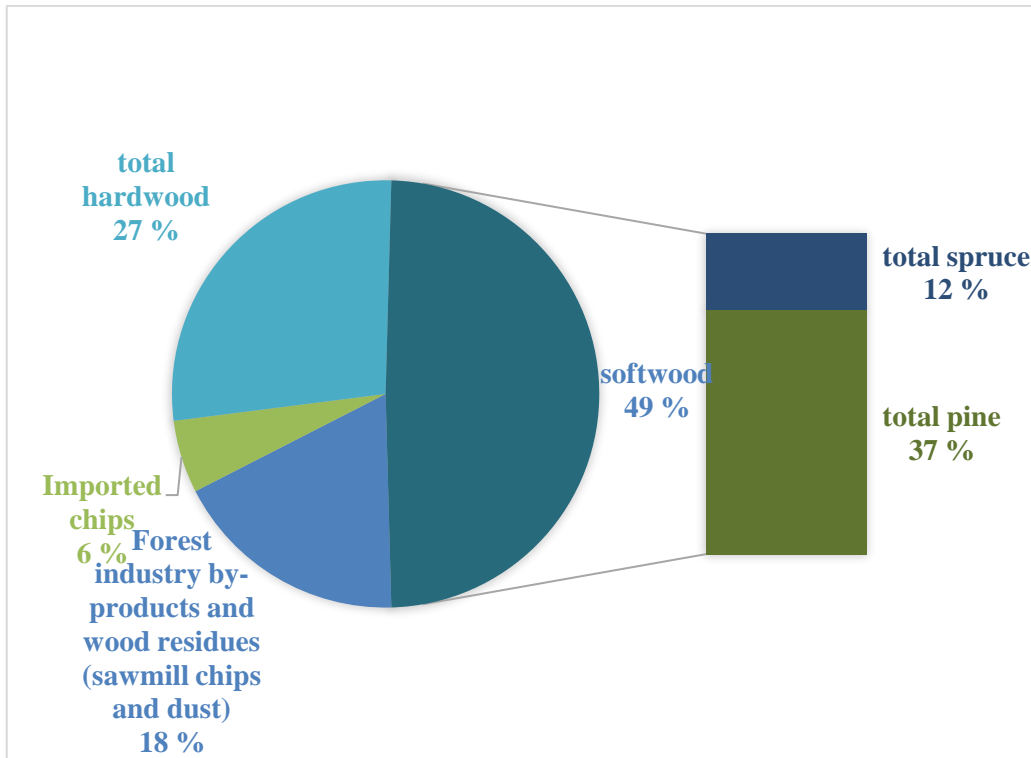


**Figure 11** Bark is debarked before pulping. (Kellomäki 2009, 21)

Direction from the outer layer bark, phloem, cambium, sapwood and heartwood. Bark is dead wood cells that protect wood. Bark has 30 – 40 % extractives from dry content and inorganics content is varying between 2 – 10 % (Jääskeläinen&Sundqvist 2007, 110).

### **2.1.2 Wood consumed in chemical pulp mills in Finland**

Natural Resources Institute Finland provides large statistical information of forest management and consumption. They have a large set of statistical tools for wood consumption in Finland. Division on chemical pulp industry wood is to pine logs, spruce logs, hardwood logs, pie pulpwood, spruce pulpwood and hardwood pulpwood. Chemical pulps also use some minor amount of imported chips and other imported resources. Sawmill chips and dust or such forest industry by products are being used as raw material in pulp mills. Logs, which are forwarded to pulp manufacturing, goes expressly to different kinds of pulp quality, instead of the regular target, sawmill. This kind of logs are usually the substandard logs and majority of these logs are unsuitable for high quality timber. In table 3 is annual (2016) wood consumption of chemical pulps of Finland. Figure 12 is a diagram made from the table 3. Almost half of the whole raw material was softwood origin.



**Figure 12** Wood raw materials in chemical pulps in Finland year 2016 (Luke, 2017)

**Table 3** Forest industries' wood consumption (1000 m<sup>3</sup>) by year, origin and assortment in chemical kraft pulp mills year 2016 (Luke, 2017).

	Pine logs	Spruce logs	Hardwood logs	Logs, total	Pine pulpwood	Spruce pulpwood	Hardwood pulpwood	Pulpwood, total	Imported chips	Roundwood, total	Forest industry by-products and wood residues (sawmill chips and dust)
2016											
Domestic wood											
..Chemical pulp industry	24	16	26	66	14,033	3,855	6,518	24,406	..	24,472	6,904
Imported wood											
..Chemical pulp industry	-	-	-	-	379	651	4,040	5,070	2,127	7,197	..
TOTAL											
..Chemical pulp industry	24	16	26	66	14,411	4,506	10,558	29,476	2,127	31,669	6,904

## 2.2 Elementary composition and macromolecular content of wood

Energy content and specific analysis of different fuels tell about these properties of energy release in redox reaction of combusting the wood. Wood compared with fossil fuels generically have lower carbon content around 49 %, table 4.

**Table 4** Wood has significant content of oxygen and hydrogen in it compared to many other fuels, like anthracite (Koch 2006, 22 originated from Haygreen & Bowyer 1982)

Elementary composition of wood	Content [%]
Carbon	49
Oxygen	44
Hydrogen	6
Nitrogen	<1
Inorganic elements	<<1

In table 4 is generalized elemental composition, wood specific depending on specie, age or growth place changes analysis results. Table 5 presents collected data from various sources about wood species properties.

**Table 5** Some collected information on wood species wood cell wall and macromolecular substance content [%] and fiber length, diameter, wall thickness and density.

	<b>Cellulose</b>	<b>Hemicelluloses</b>	<b>Lignin</b>	<b>Extractives</b>
softwoods	40 ...44	30...32	25...32	NA
spruce	42	28	28	3
pine	42	26	27	5
birch	40	37	20	3
hardwoods	40...44	15...35	18...25	NA
birch	40	37	20	3
<b>Fibre dimensions</b>	<b>length, mm [aveg., (range)]</b>	<b>Diameter <math>\mu\text{m}</math> [aveg., (range)]</b>	<b>Fiber wall thickness(earlywood/late wood)</b>	<b>density [kg/m<sup>3</sup>]</b>
Softwood	3,3, (1,0-9,0)	33, (15-60)	NA	NA
northern pine	2,9	30	2,1/5,5	390 - 420
spruce	2,9	20-30	2,3/4,5	380 - 390
Hardwood	1,0, (0,3-2,5)	20, (10-45)	NA	
birch	1,1, (0,8-1,8)	22, (18-36)	3	510
aspen	1,2	20	4,3	350

Interesting fact from the table 5 is that early wood has totally different fiber dimensions than a later wood. In usual context, wood is lodged in late wood conditions and values presented are late wood properties, for this thesis fiber dimensions are less important.

### 2.3 Spent kraft liquors from different wood species and composition

As explained in Section 2.1 wood species dry wood has varying chemical composition, then after cooking process resulting spent kraft liquor from different wood species has different content too. In table 6 are main components in the spent liquor from kraft pulping for the two main wood species pine and birch. These values are kg/ton of pulp produced.

**Table 6** Two main trees used in mill and spent liquor characteristics as approximate values kg per produced ton of pulp (Gellerstedt 2009, 184).

<b>Component</b>	<b>Pine</b>	<b>Birch</b>
<b>Lignin</b>	490	330
<b>Carbohydrate derived</b>		
- <i>Hydroxy acids</i>	320	230
- <i>Acetic acids</i>	50	120
- <i>Formic acids</i>	80	50
<b>Turpentine</b>	10	–
<b>Resin and/or fatty acids</b>	50	40
<b>Misch. products</b>	60	80

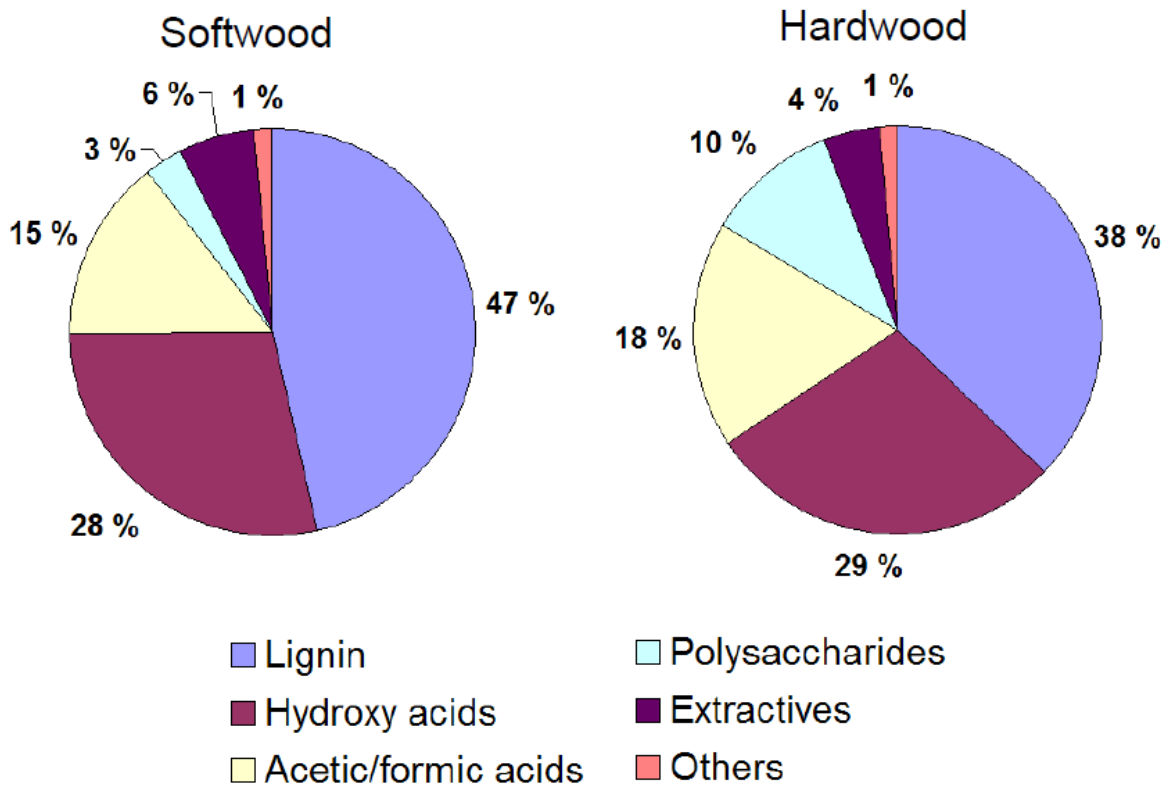
In table 6 it is noticed that birch has no turpentine content and lignin content of pines liquor is higher in proposition. Turpentine is calculated from digester relief condensates (Sjöström 1993, 241). More specific distribution of the organic material in softwood (pine) and hardwood (birch) kraft black liquor is presented in table 7.



**Table 7** Pines and birches kraft black liquors dry solids typical distribution to organic chemical components (Sjöström 1993, 158; Krotscheck&Sixta 2006, 968; Alén et al. 1992, 337; Alén 1998)

Fraction/Component	Content (% of dry solids)	Content (% of dry solids)
	<i>Pinus sylvestris</i>	<i>Betula pendula</i>
Lignin	46	38,0
Hydroxy acids		
Glycolic	3	2,8
Lactic	4,5	2,8
3,4-Dideoxypentonic	3	1,4
Glucosaccharinic	10,5	4,2
2-Hydroxybutonic	1,5	7,0
3-Deoxypentonic	1,5	1,4
Xylosaccharinic	1,5	2,8
Others	4,5	4,2
Formic acids	8	5,6
Acetic Acids	5	12,7
Extractives	7	4,5-5,6
Other components	4	11,3-12,4

Inorganics in black liquors are typically 28 % from the total amount mass content, where sodium bound to organics is 12% and inorganic compounds 16% (Krotscheck&Sixta 2006, 968). Figure 13 pie chart is one general approach to hardwood and softwood organic constituents of black liquor.



**Figure 13** Diagram presenting distribution of black liquor organics, approximated (Niemelä et al. 2010).

As hard wood species has different chemical composition than softwood species therefore compounds and quantities in the flue gases are different. In addition, one reminder is that processes are not perfect in matter of dissolving chemical pulp (cellulose) perfectly. Black liquor contains some trace amounts or smaller amounts of cellulose and hemicellulose and after pulping produced chemical pulp contains some trace amounts or smaller amounts of lignin and hemicellulose. Uncertainty is that the actual content of the black liquor in every pulp mill varies and is modified during running the pulper. Resulting black liquor from Scandinavian wood species is presented in table 8.

**Table 8** Scandinavian wood based black liquors. (Vakkilainen 1999, 15)

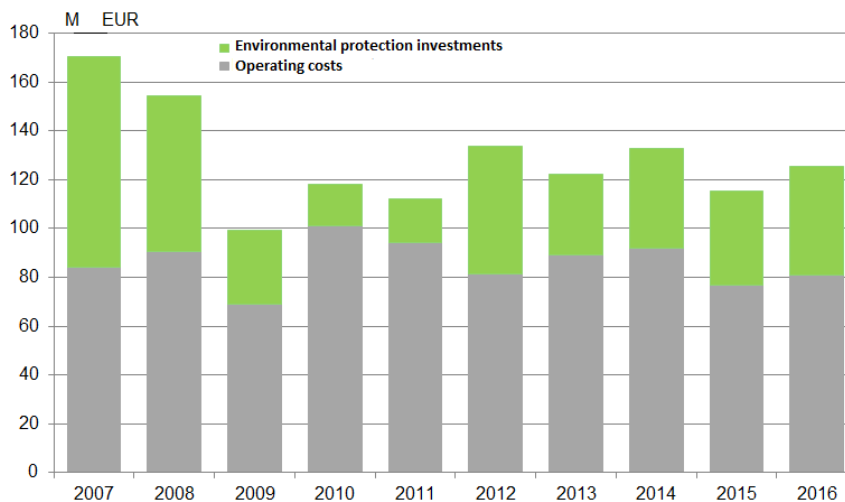
	Softwood (pine)		Hardwood (birch)	
	Typical	Range	Typical	Range
Carbon, %	35.0	32–37	32.5	31–35
Hydrogen, %	3.6	3.2–3.7	3.3	3.2–3.5
Nitrogen, %	0.1	0.06–0.12	0.2	0.14–0.2
Oxygen, %	33.9	33–36	35.5	33–37
Sodium, %	19.0	18–22	19.8	18–22
Potassium, %	2.2	1.5–2.5	2.0	1.5–2.5
Sulfur, %	5.5	4–7	6.0	4–7
Chlorine, %	0.5	0.1–0.8	0.5	0.1–0.8
Inert, %	0.2	0.1–0.3	0.2	0.1–0.3
Total, %	100.0		100.0	

Those values presented in the table 8 are good estimates for combustion calculation in Scandinavian kraft pulp mills. In Appendix II presented wood composition is used in calculation.

### 3 PULP MILL ENVIRONMENT AND FLUE GAS EMISSIONS

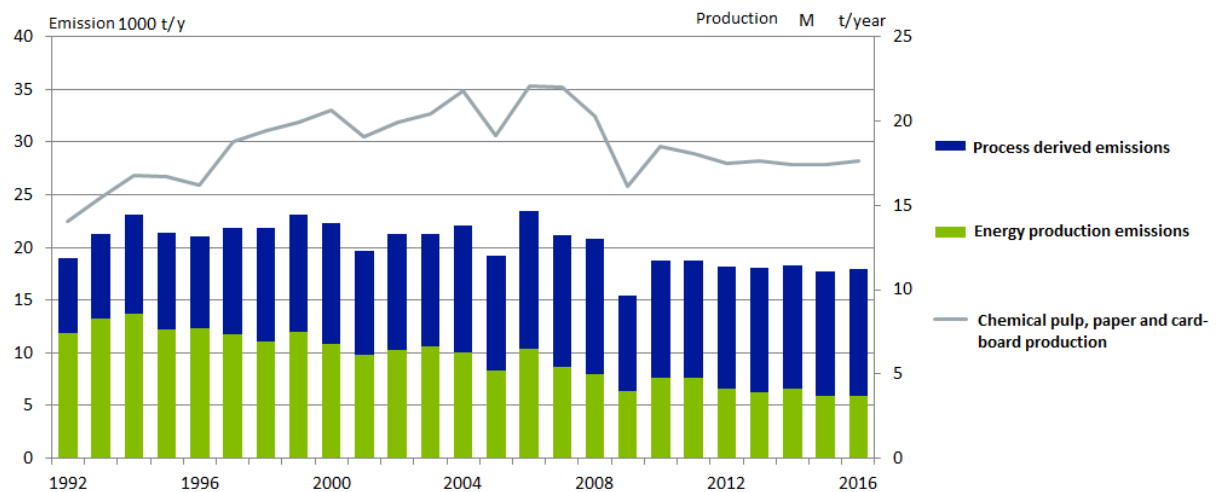
Forest industry is investment intensive business. In industry, like pulp industry, energy efficiency plays a crucial role, use of big data and industrial internet have great significance on making revenues from the work. Many research programs are currently going on around bioeconomy and forest industries. This research work is about flue gases from the RB, which are released to the environment through a tall stack in a kraft pulp mill. Calculations on combustion gas depend on the amount of black liquor to be burned and the content of the black liquor, Section 2.3.

Certain terms are synonyms for each other; stack gas, flue gas, exit gas, combustion gas and chimney gas. In here all mean similar gaseous emissions exiting a stack into the surrounding atmosphere. Monitoring is a key in industrial air pollution control and measurement. In Finland, forest industry spent quite an amount in environmental protection. From year 2007 to 2016 on average 150 million euro was spent per year to the environmental protection technologies and maintenance. Figure 14 presents the years 2007 to the year 2016 environmental protection expenses in Finnish forest industry. Operational costs cover all the costs during operation of air pollution control devices and investments include R&D in environmental field together with actual investments. Environmental protection investments include waste management, water, air and other environmentally needful investments in industry.



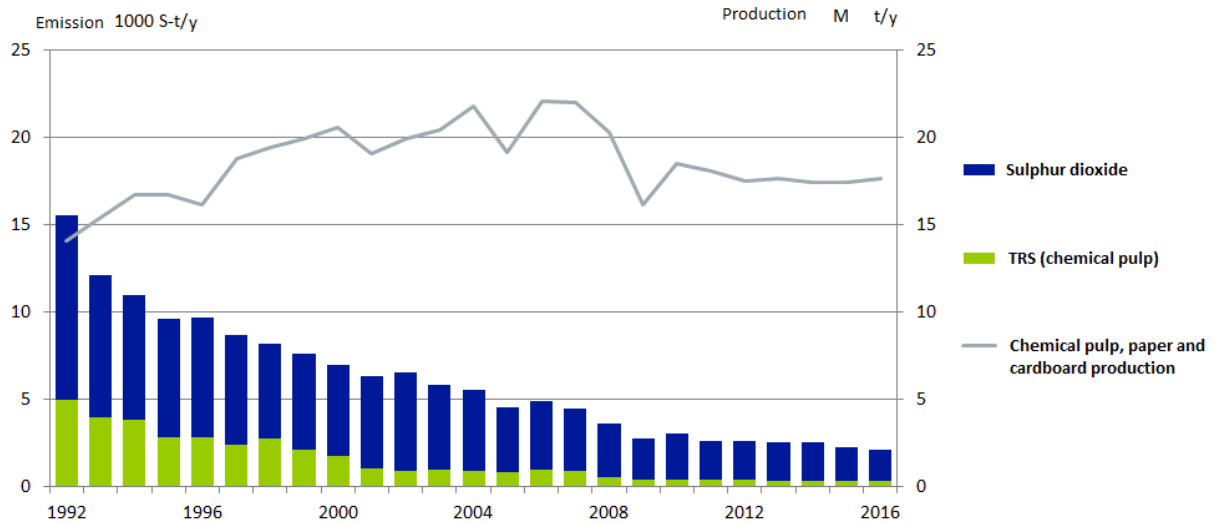
**Figure 14** Forest industry Finland spends continually money to environmental protection on its mills and other related activities. (Finnish Forest Industries 2017).

These investments to environmental protection have had influence, air emissions have reduced from year to year. Historically it is known that often malodorous gases would have been recorded from near pulp mills by nearby dwellers and some bad reputation of area still exists due to smells, while now situation is much improved. Investments to air pollution control and measurement of these atmospheric emissions have been handled efficiently well. Later years Finland had less air pollution from its forest industry. Sulphur gaseous emissions are significantly reduced as can be seen in figure 16, which Finnish Forest Industries have made from year 1992 to year 2016. Nitrogen oxide air emissions are much more difficult to be lowered, but especially energy production has been lowering its emissions to the atmospheric air.



**Figure 15** Nitrogen oxide emissions yearly 1992 – 2016. (Finnish Forest Industries 2017).

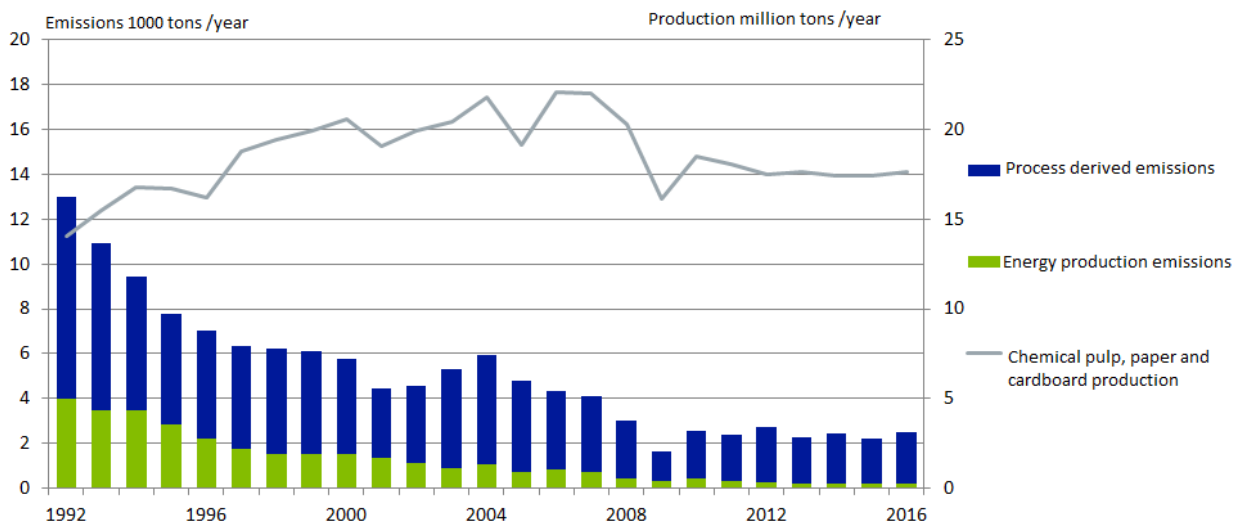
Nitrogen oxides did not have a drastic drop, but improvements are made, figure 15. Nitrogen oxides are a function of combustion efficiencies and furnace temperatures, therefore achieving higher efficiencies in power plant thermodynamic cycle is a trade between power efficiency and polluting effects of nitrogen oxides.



**Figure 16** Sulphur gaseous emissions have been successfully reduced during the years. (Finnish Forest Industries 2017)

In figure 16 are sulphur gaseous emissions in recent years of operation in forest industries. Sulphurous emissions have been reduced significantly from the past. Specially TRS, that is related strongly to odours, was lowered.

Figure 17 shows particulate matter (PM) emission reduction in the past 24 years in Finnish forest energy. Particulates are captured out from the flue gas by an electrostatic precipitator.



**Figure 17** Emission of particulate matter in the Finnish forest industry years 1992 – 2016. (Finnish Forest Industries. 2017)

## **3.1 Kraft process mills**

### **3.1.1 Recovery system**

Functions of recovery system are

- inorganic pulping chemicals recovery
- incineration; energy content recovery from dissolved organic material
- organic by-products capture (tall oil)
- prevention and control of pollutants. without recovery system waste water load would be higher inside the mills environment and as well as emissions to air

Important to discussion to this thesis is the last point, which signifies that RB releases emissions, but without operation would cause even more emissions in paper production as first three points are products. Greatly emphasized in this thesis is that recoverable black liquor makes kraft pulp mills self-sufficient in heat and electric energy. Organic by-products are turpentine, tall oil and methanol and those can have an economical boost to the economy. To remind recovery systems main processes in recovery cycle are evaporating black liquor water (raising the dry solids content), incineration of the evaporated liquors in a RB and causticizing, this includes the lime regeneration. (BREF PP 2015, 204)

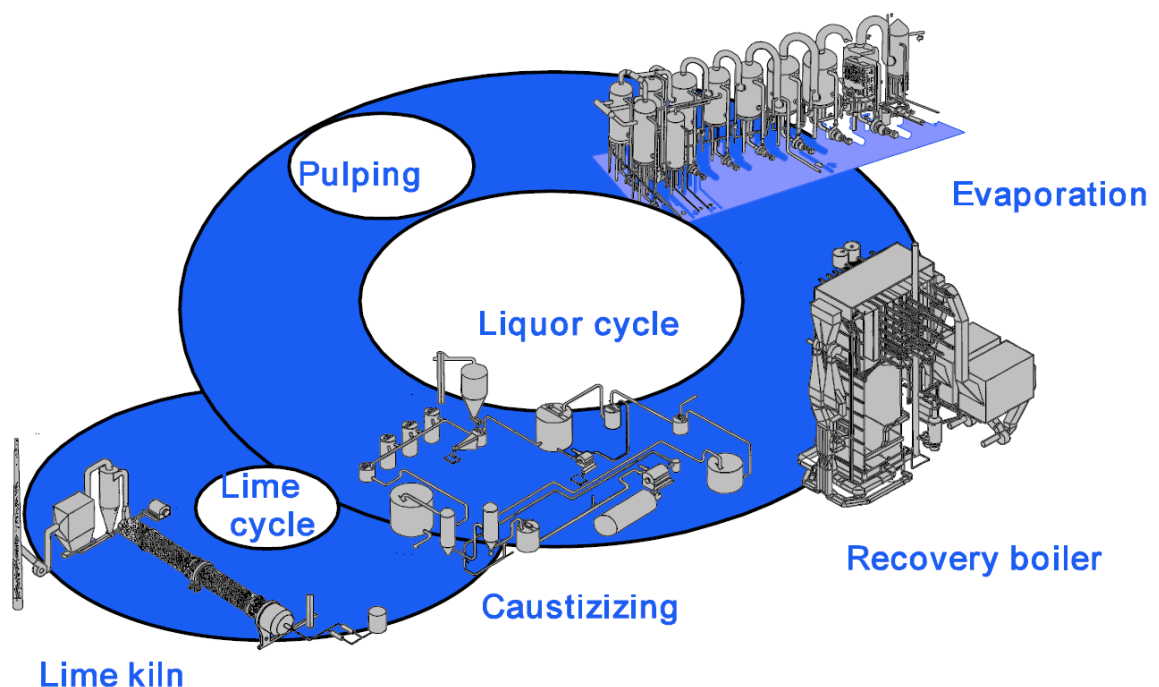
### **3.1.2 Total sulphur and higher solids content of the black liquor**

For an effective reduction of both TRS and SO<sub>2</sub> emissions black liquor is to be fired in a higher dry solids content. Comparing with the CNCG combined the fuel oil burned black liquor combustion is a more significant source of SO<sub>2</sub>. SO<sub>2</sub> is formed in mainly through the oxidation of H<sub>2</sub>S and carbonyl sulphide in the lower furnace. Black liquor is the major source for these sulphurous gas emissions. Higher dry solids content makes higher temperature, air is supplied and mixed well with fuel, where emissions are lower.

Nitrogen oxides NO<sub>x</sub> are reported and calculated with given parameter, combustion gas amount, real oxygen content and the reference oxygen content. Yearly averages are 120 – 200 mg/Nm<sup>3</sup> (BREF PP 2015, 795). Increased dry solids content of the black liquor has increased proportional NO<sub>x</sub> concentration in the flue gases.

Bioenergy is at the moment the largest source of renewable energy consumed in Finland. Bioenergy is mainly wood-derived fuels. In the point of power plants losses or energy analyst flue gases exiting a boiler are a loss. Heat and power generation using biomass is part of biorefinerys working environment.

Kraft mills use the sulphate process. Pulp making, paper making, cardboard manufacturing, timber or modern biorefining type of bio-based products and biofuels are well defined and explained in literature. Finnish forest industries have moved towards traditional timber and pulp in production. Pulp mills include a lime kiln, white liquor preparation (causticizing), bark combustion facilities, evaporator, cooking and washing. Figure 18 represents the general cycle of kraft recovery cycle.

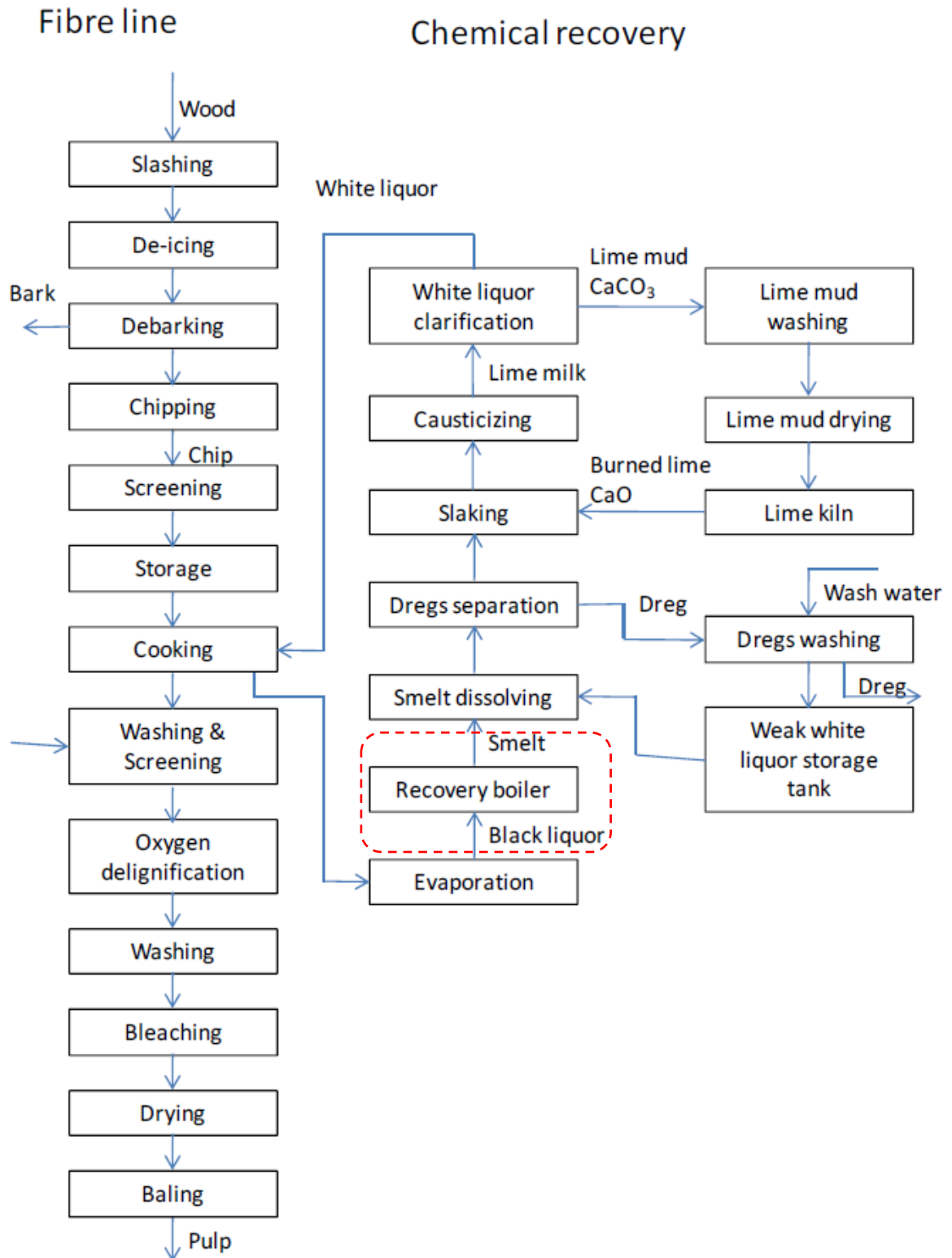


**Figure 18** Cycles of kraft recovery (Kivistö&Vakkilainen 2010, 58)



Odorous gases from all the cycle parts are forwarded to combustion. Disposal of odorous vent gases from all areas of the pulp mill is needed for sufficient operation (Krotscheck&Sixta 2006, 974). Figure 19 shows all the steps of making chemical pulp. On every mill are varieties in the unit processes in fibre line as well in the chemical recovery. Data of black liquor quality as well as furnace output smelt can be obtained through analyses.

Pulp has a reputation of bad odour releases by the public. The odour is caused by some of the sulphur containing gases and they are low threshold gases to be detected by human. Some of these malodorous gases are because of decaying organic and biological matter. Decomposition is done in favourable conditions by decaying and putrefying bacteria. RB is commonly one source of these gases (TRS). Levels of concentration of these gases might be lower and “safe” for human breathing in, but nuisance by some public is possible to notice. (BREF PP 15, 189).



**Figure 19** The chemical pulping process and RB placement in red. In the courtesy of (Kivistö&Vakkilainen 2010, 33)

The focus due to limits of the thesis is marked off red in figure 19. RB burns black liquor to recover chemicals used in pulping and produce steam by burning organic matter to make

electricity, process heat used at operation of the mill. External heat and power will be sold out to the consumers. RBs in Finland have a significant role in the electricity market as they are base-load power stations in the electricity grid mix. District heating in Finland is necessary in colder months to keep housing warm, RB produces hot water to the district heating pipeline. RB boiler might not work as external heat supplier in the tropical communities, where district heating market is low. Odorous gases from the pulping processes will be burned to simpler compounds. After combustion there is smelt, which contains inorganics used sodium sulphite ( $\text{Na}_2\text{S}$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and unburned organics and trace compounds (Kivistö&Vakkilainen 2010, 60–61). Knowingly, the world is changing rapidly, so is forest products yields and biofuels high combustion efficiency the goal for utilizing most of the available mass and energy. Higher dry solids content gives better results in combustion and recovery of chemicals.  $\text{NaS}_2$  and  $\text{NaOH}$  are the cooking chemicals.

### **3.2 Influencing factors affecting pulp mill combustion gas amount**

Largest flue gas flows are from RB. Lime kiln has lower flows of material to the boiler than RB. As given by reported value for RB flows are range of 4625 – 8250  $\text{Nm}^3/\text{ADt}$  lime kiln has values of 303 – 1000  $\text{Nm}^3/\text{ADt}$  (not reported in the same reference oxygen level). Given values from officials should be correct. Production is either lower than capacity or higher than assumed. There are various reasons why pulp mills emissions or flows are affected. Wood species influence was described in Chapter 2.

#### **3.2.1 Yield of chemical pulp**

Yield of pulp means the mass fraction of the incoming wood that is converted to pulp in mills. The higher the yield of the chemical pulp, the lower are the flue gases per ADt. Also for economic reasons the mills want to have the highest possible yield from the wood that they have bought. This is an economical question also and yields are not reported along other monitored numbers from the pulp mills. There is a possibility to estimate the yield by knowing the exact flue gas flow.

The higher amount of cellulose on wood, depending on species the higher the yield also. Here we should compare different wood species and do some balances on them. Pine, birch and spruce are mainly used in Finnish conditions.

Estimated values for bleached Nordic softwood are around 44 – 46 % and hardwood 47 – 49 %. Eucalyptus has higher yield 51 – 54 % (BREF PP 2015, 110). Varying results for yield are because some mills produce more pulp than the other (BREF PP 2015, 249). Wood species and their differences in yield have an effect on the result of NO<sub>x</sub> emissions per tonne also specific water borne emissions are lower.

### **3.2.2 Process**

By process is meant the whole mills material balances, which are affected by the age of the equipment, cooking and chemicals, water circulation and water management. Age of equipment is every unit's age. Bleaching-, cooking- and water chemicals can vary and have influence also to the level of closure in water system in the mill and amount of the biosludge. As well as recovery units own operation combustion properties and water content of black liquor. Biological treatment at a waste water treatment plant dissolved organic matter converts to biomass, which then is sludge. It is constituent of different kind of – fiber sludge is from pre-sedimentation tank, excess sludge from activated sludge plant, dewatered sludge may be combusted in bark boiler or some cases in RB. In the future biogas plants will take care of this type of biomass. (BREF PP 2015, 102)

It should be reminded that there are on-site power plants, auxiliary burners and CHP that add amount of released emissions to air (BREF PP 2015, 254). In this research only RB's emissions to air are under study. Collecting the malodorous gases from the whole mill is made and are forwarded to treatment, treatment is often oxidation in RB. Diffuse emissions of these sulphur containing gases should be avoided and monitored by the staff (BREF PP 2015, 254).

### **3.2.3 Boiler overload and buffering tanks**

RB is designed to a certain point, where running combustion is better for many reasons. If overloading occurs SO<sub>2</sub> concentration rises. Buffering incoming hot liquids in large enough capacity storage tank helps in controlling flow inside to the RB. It is said that modern kraft pulp mills are more than self-sufficient in heat and electricity (BREF PP 2015, 204).

### **3.2.4 By-product recovery and handling**

Overload problems could be avoided in the future by increasing mass and sorts of by-products, especially separated lignin by-products. Other by-products such as tall oil soap, turpentine, bark, methanol, sulphuric acid, biogas or product gas depending on mill can be recovered or fired. By-product separation and extraction reduces combustion gas flow from the RB if compared to a case without.

## **4 REPORTING AND MEASURING FLUE GAS FLOW AND EMISSION LEVELS ASSOCIATED**

### **4.1 Reporting emissions and technical influences to atmospheric flows**

Reporting emissions is done by the company, they have to conclude an environmental report from the emissions from the pulp mills environment. Technical issues influence to the atmospheric pollution levels as well composition of the flue gas. Such technical devices and methods are scrubbers, boilers burn control and those have simultaneous impacts on the direct measurement.

Industrial emissions directive 2010/75/EU is one directive inside EU that does determine RB's operation lawfulness.

Best Available Techniques reference document (BREF) is the document that most of the mills follow accordingly. BREF has several suggestions to make industrial emissions lower in making certain things. First of all energy consumption of pulp and paper production sector is significant and verifying emissions is a key to make conclusions on where certain mills efficiencies level off. Pulp and paper consumes 5,7% of total industrial energy use. Heat energy goes to the heating of water, wood chips, pulp fibres, air and chemicals to process temperature, cooking liquor heating, evaporating water from spent kraft pulping liquors in the evaporators before the firing, evaporating water from pulp or paper sheet in the paper/pulp machine dryer and drying of coated paper. Electrical power is consumed by pulp beating and refining, drives for machines and other pulp and paper machinery, transports with pumps, fans, belt and screw conveyors, fluid and suspension mixing, on site chemical preparation, vacuum pumps, compressors. Increased specific electricity consumption is proven to be due to higher quality requirements of paper, increased speeds in paper machines, new pressing and drying technologies (reduced heat demand though) and tightened environmental requirements (control techniques in waste water treatment and flue gas cleaning). This thesis emphasizes the need for advanced process monitoring for smooth operation where energy efficiency and pulp production is better. (BREF PP 2015, 76)

Usually announced measurement results are reported in pulp mills reporting in the form of  $\text{kg}_{\text{pollutant}}/\text{ADt}$ . Annual averages will be reported yearly by summing all the masses, for each time period measured. ADt means air-dry ton of chemical pulp that has 900 kg of bone dry cellulose fibre content and 10% moisture content. Concentration amounts can also be reported as  $\text{mg}/\text{m}^3$  for a certain pollutant again typically as annual average. Flue gas flow per air-dry ton of chemical pulp ( $\text{Nm}^3/\text{ADt}$ ) is not typically reported in EMAS or public reports. It is possible to have ton-of-pulp specific value as well pollutant mass per volumetric flue gas flow by dividing annual total pollutant mass flows by annual total pulp production.

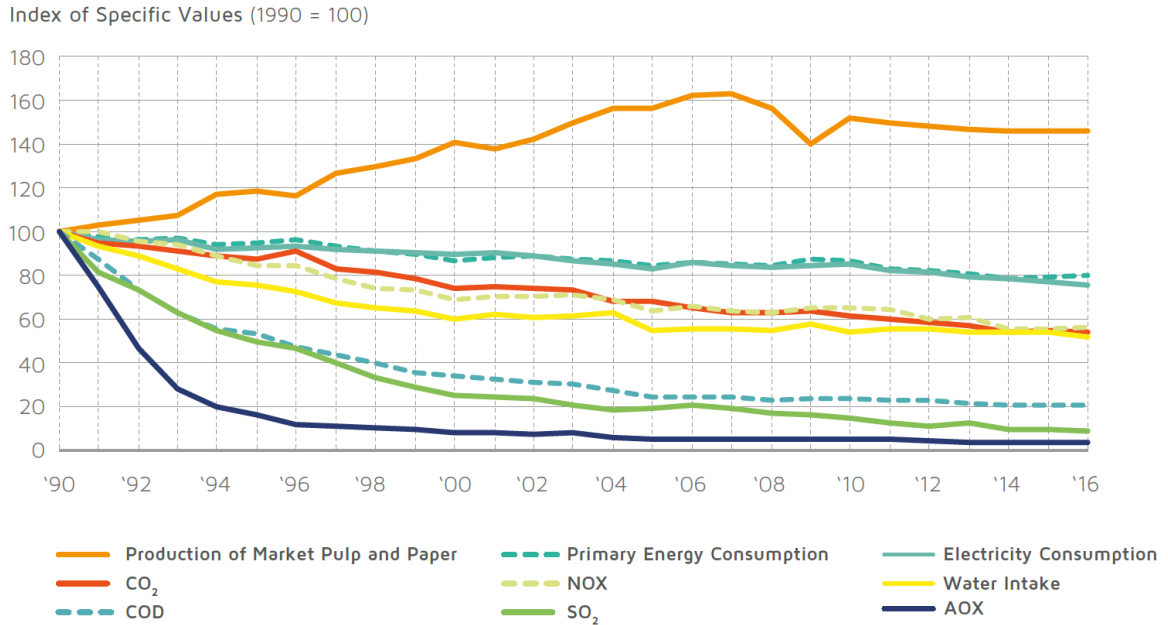
The following equation 1 gives relation between the main parameters for estimating annual load of the chemical species emitted (Brinkmann et al. 2018, 63).

$$E = Q \times c/100 \times \left(\frac{M_w}{M_{WE}}\right) \times t \times (100 - R) \quad (1)$$

where

- $E$  is annual load of the chemical species emitted (kg/yr)
- $Q$  is the fuel mass flow rate (kg/h)
- $c$  is concentration of the elemental pollutant in the fuel
- $M_w$  is molecular weight of the chemical species emitted (g/mol)
- $M_{WE}$  is elemental weight of the pollutant in the fuel (g/mol)
- $t$  is operating hours (h/yr)
- $R$  is retention factor (wt-%) mass fraction of the elemental pollutant remaining in the combustion process

Confederation of European Paper industries (CEPI) publishes Key statistics annually to give aspect the whole pulp and paper production. In figure 20 is presented an environmental impact of the CEPI industries. Index is done from the year 1990. Changes have been smaller seemingly in later years, maybe the index should be transferred to closer year than 1990. Indexes are being made by help of equation 1.



**Figure 20** Evolution of Environmental Impacts of the CEPI Pulp and Paper Industry

Coming towards 2020 it should be recognized that more suitable starting year for such diagrams as figure 20 could be from the year 2005, as that year first Conference of the Parties serving as the meeting of the Parties to the Kyoto Protocol (CMP) CMP 1 was held. CEPI is not publishing the main value for the matter of this thesis, Nm<sup>3</sup>/ADt (dry condition, 6% oxygen content), which could be modified to the similar index of specific value hopefully in the future.

#### 4.1.1 Averaging emissions to air and key parameters

For averaging the air emissions, it is needed to make clarification, how exactly averaging will be done correct. Table 9 explains daily average, average over the sampling period and annual average.



**Table 9** Emissions to air and averaging periods (2014/687/EU, 81)

<b>Daily average</b>	Average over a period of 24 hours based on valid hourly averages from continuous measurement
<b>Average over the sampling period</b>	Average value of three consecutive measurements of at least 30 minutes each
<b>Yearly average</b>	In the case of continuous measurement: average of all valid hourly averages. In the case of periodic measurements: average of all ‘averages over the sampling period’ obtained during one year.

Table 9 presented yearly average has two different cases that apply, in case of an automatic measurement system (AMS) all valid hourly averages are averaged and periodic samples are averaged from the sampling periods.

#### 4.1.2 Reporting of RB flue gas flow and pollutant concentrations

For pollutant mass concentrations  $\text{mg}/\text{m}^3\text{n}$  is value. These values should be referred that they are in standard condition (refer to  $\text{Nm}^3$  or  $\text{m}^3\text{n}$  273,15 K and 101,3 kPa), oxygen content and if water vapour is included in the volume (dry/wet). Water vapour is commonly deducted, but should always be notified. RB in Finland has reference oxygen content of 6%. Equation 2 presents way of changing concentrations from measured oxygen level to another. (BREF PP 2015, 58)

$$E_r = \left| \frac{21 - O_r}{21 - O_m} \right| \times E_m \quad (2)$$

where  $E_r$  emission concentration in reference state ( $\text{mg}/\text{m}^3\text{n}$ )  
 $O_r$  is reference oxygen level (vol-%)  
 $E_m$  is emissions concentration in measured oxygen ( $\text{mg}/\text{m}^3\text{n}$ )  
 $O_m$  is measured oxygen level in RB duct (vol-%)

For calculating the flue gas flow in the reference oxygen level equation 3.

$$\dot{V}_r = \left| \frac{21 - O_m}{21 - O_r} \right| \times \dot{V}_m \quad (3)$$

where  $\dot{V}_r$  is standard condition volumetric flue gas in reference oxygen (Nm<sup>3</sup>)  
 $\dot{V}_m$  is standard condition volumetric flue gas amount in measured oxygen content, real excess oxygen in % during operation (Nm<sup>3</sup>)

As can be seen in equation 3, if reference oxygen content is higher than the measured content, volume raises. Measurement methods vary over Europe as well reference oxygen content. In Finland RB and lime kiln are in 6 % reference oxygen content and separate burner for odorous gases in 3 %. In comparison of emission levels, it is essential that the oxygen content is same, especially when comparing between countries, different mills or different burners.

Following table 10 gives good closure to interrelations for concentration and specific emissions. This gives way of changing (as reported emission loads should be consistent) from unit mg/Nm<sup>3</sup> to kg/ADt.

**Table 10** Conversion of air pollutant from concentration rates to specific rates.

measured targeted emissions concentration in one year mg/Nm <sup>3</sup>	<b>a</b>
value from continuous monitoring of concentration, sum of values that are valid mg/Nm <sup>3</sup>	<b>b</b>
flue gas flow rate an on hourly basis Nm <sup>3</sup> /hour	<b>c</b>
annual operating time (hours/year)	<b>d</b>
annual off-gas volume Nm <sup>3</sup> /year	<b>e = c×d</b>
pollutant mass per year (kg of pollutant per year)	<b>f = b×e</b>
annual net production (ADt of pulp/year)	<b>g</b>
specific emission factor (kg/ADt)	<b>i = f/g</b>
specific flue gas volume (Nm <sup>3</sup> )	<b>h = e/g</b>

The calculation of specific loads need the following initial data.

- concentration of pollutant on an annual average (mg/Nm<sup>3</sup>)
- exit gas flow rate on an hourly basis (Nm<sup>3</sup>/h)
- annual operating time (hours/year)
- annual net production (ADt of pulp/year)

#### **4.1.3 Continuous measurement and periodical measurements**

Relevant parameters for a certain measurement component are pressure, temperature, oxygen, CO and water vapour content in flue-gas for combustion processes. Simultaneous and on same time-frame reported data gives a more accurate result for others such as exit gas flow and concentration values. If there is other parameter monitored only periodically and the other continuously, mathematically considered results are not dependable enough.

As mentioned before in table 10 emission load to air is a result of two things, the simultaneous measurement of the concentration and the corresponding average of volumetric flow rate under the standard condition and reference oxygen content. Operational time is reported with comparable emission loads. (BREF PP 2015, 42)

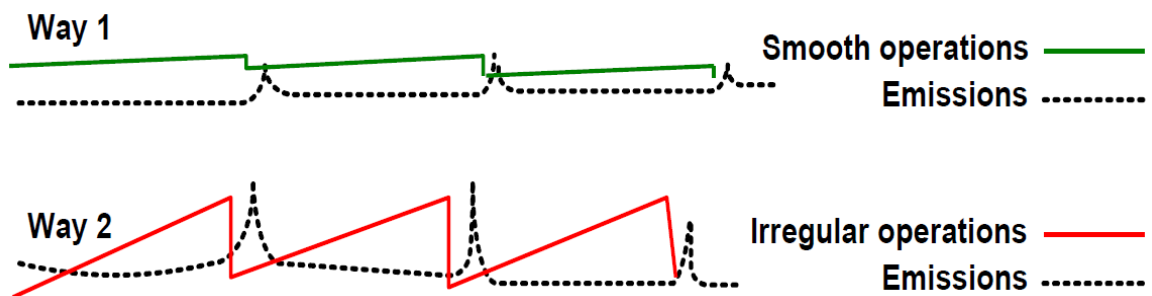
Finland has great variety of options in monitoring for flow fuel analysis, continuously monitored or periodical measurement are implied. Fuel analysis is a mathematical model (C,H,O,N,S, ash, moisture and energy content are used as data input), Appendix II contains an example of the model of combustion for hardwood and softwood. Table 11 shows collected methods in Finland for RB. (BREF PP 2015, 52–54).

**Table 11** Adapted from BREF PP 2015, 54

Parameter	Recovery boilers typical monitoring systems in Finland
Flow	fuel analysis, continuously monitored, periodical measurement
SO <sub>2</sub>	continuously monitored, periodical measurement
TRS or H <sub>2</sub> S	continuously monitored, periodical measurement
NO <sub>x</sub>	continuously monitored, periodical measurement
Dust	periodical measurement, (continuously trials evolving)
CO	periodical measurement
Heavy metal	periodical measurement
Dioxin/Furan	periodical measurement

It is reported that for flue gas flow in Finland ultrasonic measurement, S-type Pitot-tube and heat and mass balance are the options (BREF PP 2015, 57).

Periodical measurements are not valuating the whole operation time during the year. Smooth running of the mill adds environmental value. Material efficiency increases, pollution minimization, lowers energy consumption and reduces costs. Controversially repetitive production breaks, technical shutdowns and unplanned releases causes larger emissions, inefficiencies in processes which leads to lower product quality. (BREF PP, 2015, 168)

**Figure 21** Emission levels depend on how mill is operated (Nilsson et al. 2007, 16).

Advice from way 1 mill in figure 21 operates are given such points:

- Computer-based control systems with on-line measurements in monitoring of atmospheric emissions reduce the need for separate emission control, and additionally enable statistical follow-up. Information and automation are there.
- Monitoring of process parameters with continuous measurements demonstrates the stability of both manufacturing processes and emission control techniques, allows data to operate close to the optimum process parameters and stabilizing critical process parameter is possible.
- Optimizing production levels in relation to maximum capacity. Full capacity production rate may cause disturbances and uncertainties in emissions control.
- Facilitates should share their information, then right actions in timely manner
- Exceptional conditions should be reported
- Right planning of shutdowns and related actions

With these pre-mentioned actions unexpected peaks and accidental releases can be greatly reduced. All listed methods apply to the old mills and new ones. (BREF PP 2015, 168)

Often mills emission reports are guided to present the normal condition operation of RB. This includes change in load of boiler, normal variations in the input or process conditions, change of grade or quality, interruptions, routine maintenance, and cleaning (cleaning of filters, scrubbers or measuring system), supervision and external measurements. Start-ups and shut down periods are arranged specially. (BREF PP 2015, 41)

#### **4.1.4 Flue gas scrubber and quality of measurement results**

Flue gas scrubber usually increases the relative moisture content of the stack gas, so that concentration measures or other are not in great validity, unless dried sample is used. Flue gases from the RB are typically wet. Indirect method for evaluating flue gas flow is another possibility along direct measurement.

Mainly two reasons are typically affecting measurement results in the RB; an on-line measurement device can be covered by ash and other significant difficulty is high moisture content of the flue-gas. (JRC 2015, 52)

#### **4.1.5 Boiler efficiency and burn control**

Boiler efficiency affects to certain emission compounds. Also higher efficiency means RB's better environmental and economic performance. Higher energy efficiency lowers the amounts of additional power or heat demand. A tertiary burner burns gases fully. Flue ash contains unburned materials. Boiler efficiency and burn control is closely related to Subsection 3.2.3.

Modern RB's work in area of 3200 – 5000 tds/day (Jinhai pulp and paper in Hainan, China 7000 tsd/day and produces steam 510°C and 140 bar). (Bajpai 2017.figure 4.7 and figure 4.8).

#### **4.1.6 Certain impacts to direct measurement correctness**

Factors affecting direct measuring are quite large. As an example there must be a place to measure. Table 12 summarizes certain challenges to their contents.

When the industrial emission directive is implemented, the old measurement methods might not be sufficient anymore. Measuring point must provide good placement outside and inside of the channel. Higher elevation from the ground is needed for some of the individual measurements. Unsteadiness affects overall results. Flue gas properties vary along the changing volumetric rates in different parts of the measuring space. Even smaller componential fractions cause difficulties in order to obtain trustworthy results.

**Table 12** Instrumentation problem associated with emissions measurement in stationary sources

<b>Challenge</b>	<b>Content</b>
<b>measuring point</b>	not sufficient placement
<b>new methods in old spots</b>	old places for measurement are not designed properly
<b>unsteady process</b>	fluctuations in flow and its concentration of compounds (figure 28 )
<b>changing standard requirements</b>	Standards are regulatory and implementation is difficult in changing conditions
<b>flue gas properties</b>	moisture, lower temperatures, drying necessary
<b>smaller componential fractions</b>	PCDDs, PCDFs

## 4.2 Measurement technologies and emission measurement devices

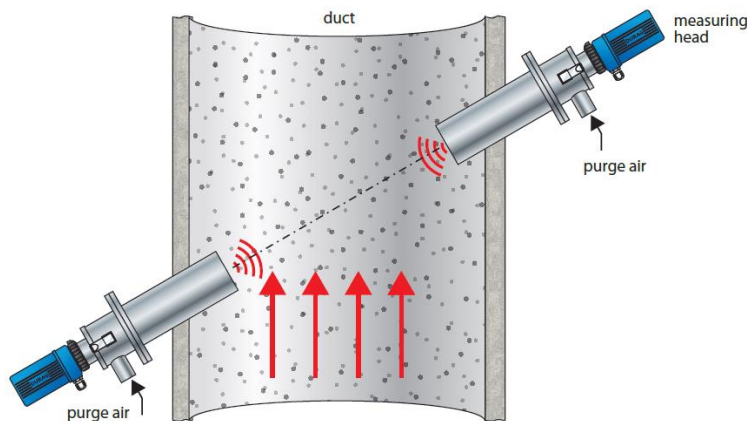
It is necessary to go through the principles of air emission measurements, for the purpose of understanding of the content of this thesis and results presented in the coming chapters. Actions and techniques apply in measurement, which are standardized. The branch of industrial emission monitoring and reporting was followed by environmental regulations that regulated the necessity for laboratories to make air pollution control measurements in industrial establishments. Also smaller plants and their installations are required to do some test for better process design and optimizing, effective functionality of air pollution control devices (APC), environmental license and QAL-2 and AST laboratories as reference results. Measuring sites may be not only in flue gas stack, other like boiler, before APC and after, not only one place is utilized as measurement device placing. In Finland environmental license is permitted by Centre for Economic Development, Transport and the Environment. Modern applied standards in Finland follow the European standards and use-precise methods. Measurement has become more complicated through new standardization. Older methods have attained proven status as defects are better understood than those of new technologies, but real-time and continuous measurement might be less affordable in case of older methods. In the United States is used EPA methods. Environmental equipment is a part

of purchase of RB, a significant increase in instrumentation markets in continuous emissions measurement is due to legal binding that GHG should be accounted as a mass unit.

Indirect and direct method are also involved if method is sampling type or then in-stack continuous type. For pollutant concentration indirect means sampling type. RB causes problems in CEMS, reason is that ash build up on a surface of measuring devices and flue gas moisture content is high (Subsection 3.2.3).

#### 4.2.1 Ultrasonic gas flow rate measurer

Maybe the most attractive and probable flow rate measurer is the ultrasonic gas flow rate measurer. Accuracy of these devices has improved in later years for gases. Non-contact measurement is better always and deposition of ashes or wearing of equipment is less.



**Figure 22** Durag D-FL 220 operating principle (Durag 2018)

#### 4.2.2 Thermal mass flow measurement sensors

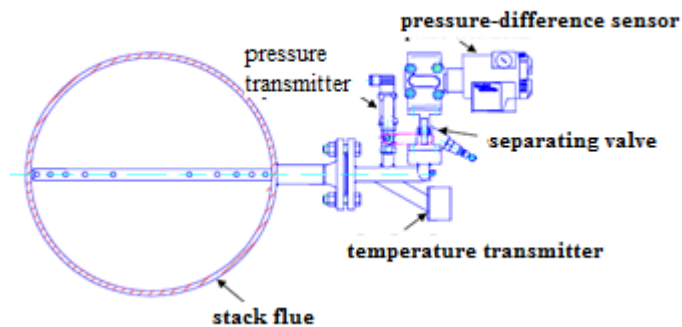
In RB's exit gases temperatures are usually higher and contain impurities, it is possible to meet the need for mass flow measurement. It is common to use thermal mass flow sensors in continuous mass flow measurement. Thermal mass flow measurement instrumentation is mainly used for gases.



Manufacturers of instrumentation for thermal mass flow sensors are for instance Kurz instruments, ABB, Sierra Instruments, FCI and many others. Thermal mass flow measurement has good accuracy (1-2 % uncertainty).

#### 4.2.3 Integrating Pitot-tube

The stack can be instrumented with averaging Pitot tube. Pitot tube is a principal differentiating pressure measurement. Integrating Pitot tube is a suitable tool for averaging pressure sensing in a duct. It has inbuilt temperature – and absolute pressure measurement. One only tube to the channel, fast and priceworthy installing, less maintenance and automatic operation on some extend are advantages of integrating Pitot tube. Figure 23 presents this device.



**Figure 23** Example of an integrating Pitot tube (Adapted from Kontram)

#### 4.2.4 Multi-gas concentration measurer

Fourier Transform Infrared FTIR is an analytical instrument for using spectroscopy to measure concentration commonly presented in ppm from purified (particulate matter removed) flue gases. FTIR consumes less time, while it may be used for several components at once and is after calibration automatic and even continuous measurer. Monitoring applied by on-line gaseous compound meters is often used. Reliability and reduced costs are the main reason for having these devices in a power plant.



A

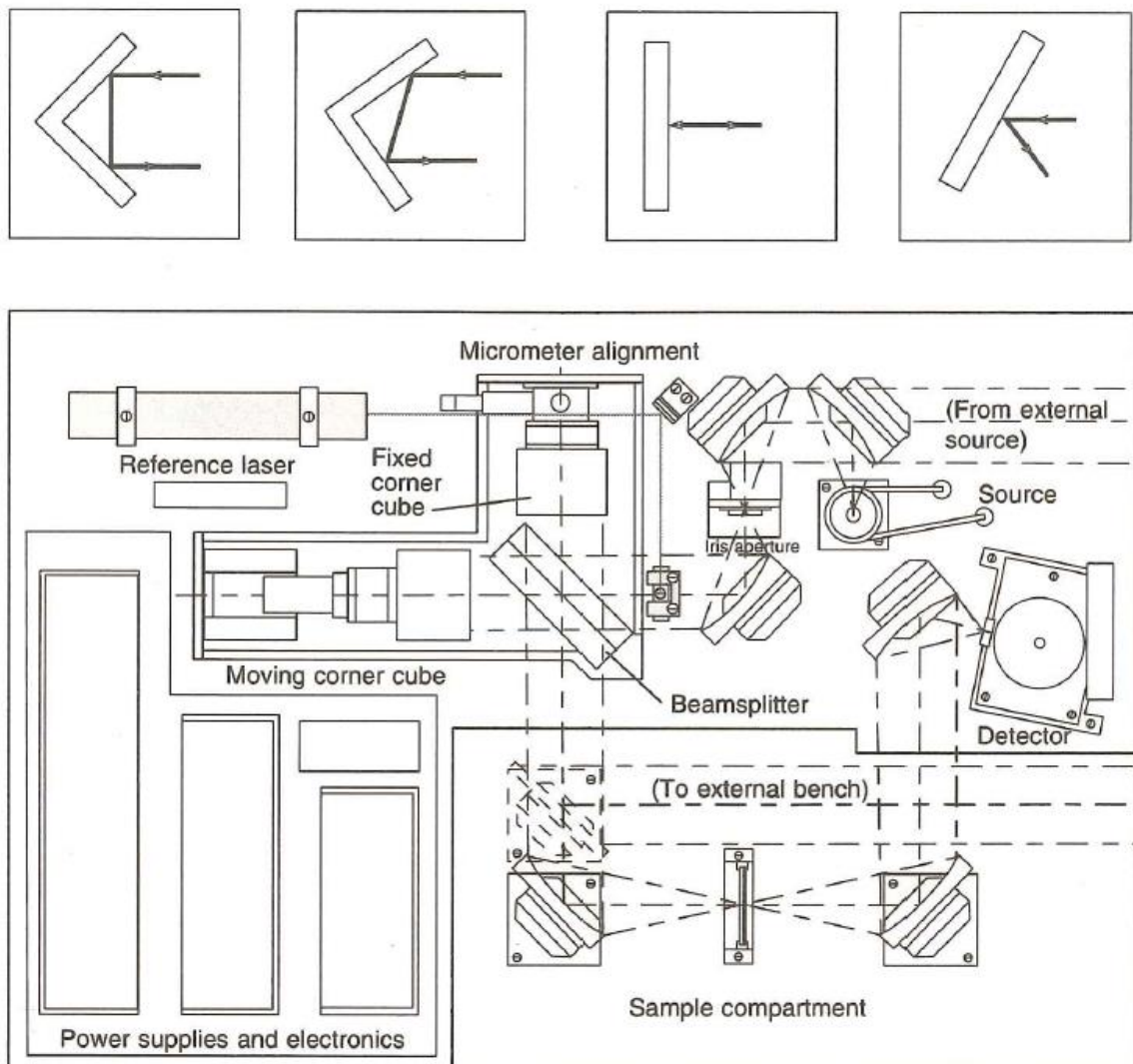


B

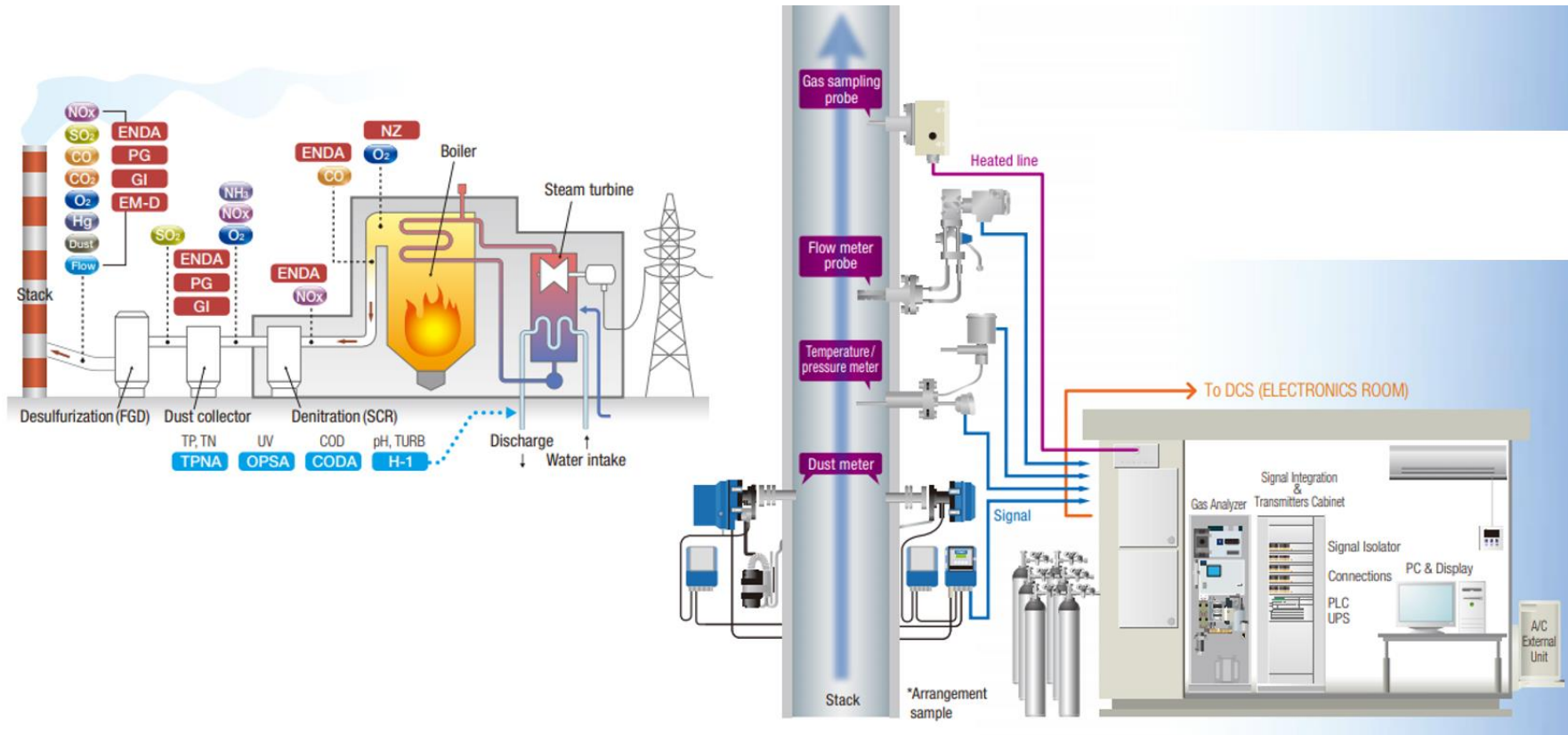
**Figure 24** Above pictures A and B show how a measurer works with the FTIR for some industrial flue gas (pictures from Gasmot Oy)

RBs use FTIR for reference measurements. FTIR is mainly working as concentration measurer. FTIR development has been recently developed considerably. Finnish company Gasmet makes FTIR devices for several purposes. They also provide the white paper for FTIR measurer to give the principles and overview to FTIR technology (Gasmet 2018).

Figure 25 presents the construction of FTIR device. It uses mirrors with certain fine mechanics and electronics. Figure 26 gives an image of the whole possible measurement field in industrial boilers and placing of the multi-concentration measurer at the last heated probe measuring point.



**Figure 25** Construction of FTIR device for measurement (Torvela. 1994, 123)



**Figure 26** Continuous emissions measurement procedures and example of all the components in industrial boilers

### 4.3 Volume rate in duct – flue gas flow

First, the nature of the flue gas flow will be verified a bit. Seemingly variation on flue gas flow is 6000 – 9000 Nm<sup>3</sup>/ADt (Dahl 2008, 125), depending on the wood species used and yield of the pulp. Advection of flue gas is happening in a duct. Swirl makes flue gas flow turbulent. Due to height, the stack flow has higher pressure in the down part of the duct compared to the higher part, where pressure is closer to surrounding ambient air. Purpose of the high stack is to get flue gases spread out from the mill area. Higher concentrations of pollutants in respiratory air have several health risks to the workers who are in a constant exposure.

Standards are implemented in measurement of duct flow. ISO 16911, which has two parts given first one for manual methods and the second one for continuous automated methods.

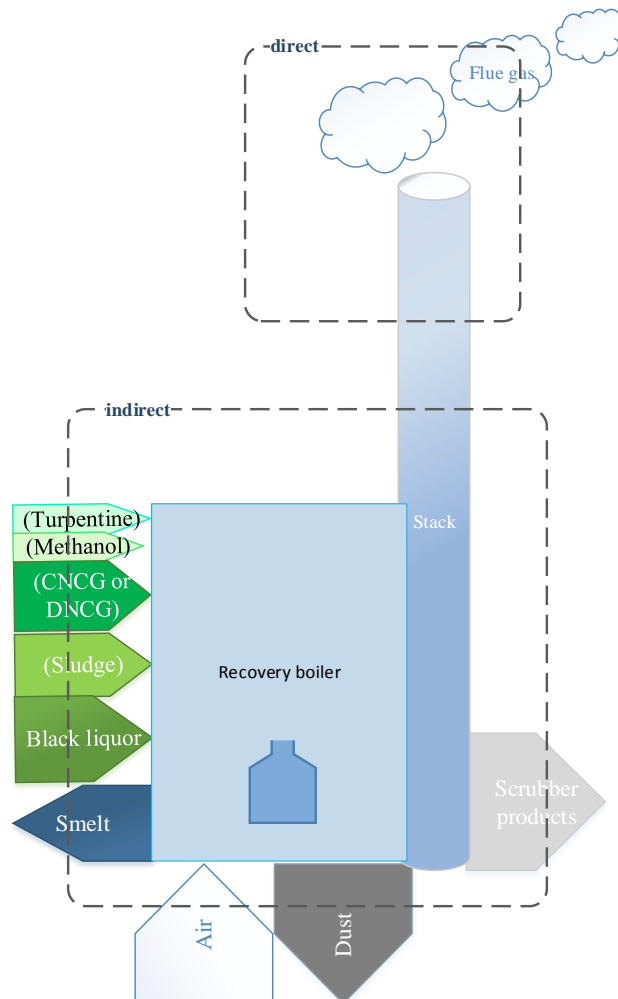
Different methods are in use of determining the flow in the duct. It can be a trace gas system or energy-mass balance computation. Still, many prefer Pitot – tube, which measures velocity of the flue gas. Pressure sensing methods are using following equation 4.

$$q_v = A\bar{v} \quad (4)$$

where  $q_v$  is volumetric flow rate  
 $A$  is area of the channel  
 $v$  is average speed of gas inside the channel

Figure 27 presents an example of boundaries to make emission balances. Certain flow of black liquor to be combusted will have certain amount of substances released in gaseous form to the stack and some end up unburned to the smelt – this is called indirect method of evaluating emissions (JRC 2017, 12). Other boundary of emission balance is one where boundary is drawn in to the stack flow and surrounding atmospheric air – this is called direct method. Direct method means usage of measuring instruments (JRC 2017, 12). Reported values from the mills varies, some are done by indirect method, and some are done by measuring.

Reference Document on Monitoring of Emissions to Air and Water from IED Installations (2018) flow rate is measured by standard EN ISO 16911-1: 2013 for periodic measurement and CEN/TR 17078: 2017 include guidance on the application of the standard. Here monitoring methods include differential pressure (Pitot-tube), vane anemometer, tracer dilution, tracer transit time and calculation from energy consumption. For continuous metering are generic standards and EN ISO 16911-2: 2013. Standard reference standard is EN ISO 16911-1: 2013. Continuous flow rate measurement methods are ultra sound, differential pressure, IR cross-correlation of turbulence and thermal mass flow. Reference standards to EN ISO 16911-2: 2013 are EN 15267-14:2009, EN 15267-2: 2009, EN 15267-3:2007 and EN 14181:2014.

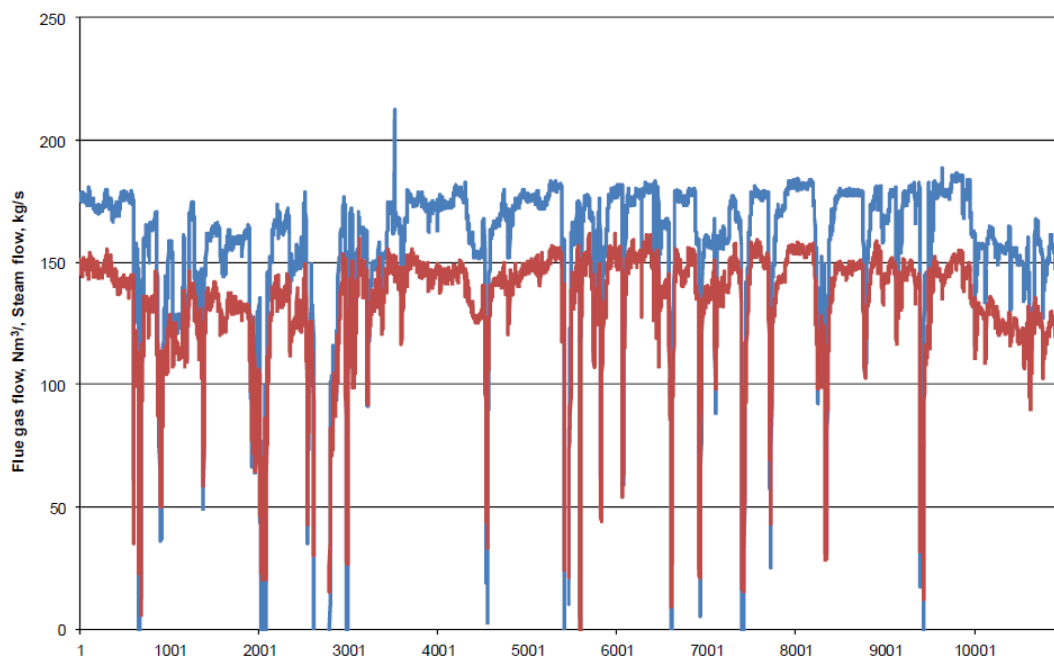


**Figure 27** Examples of boundaries in RB to environment and emissions measurement – the direct and indirect method for flue gas flow

Remarks in figure 27 that standard condition flue gas flow may be calculated indirectly or directly. Indirect is not using any devices in the duct.

#### 4.3.1 Uncertainties in the flow rate measurement of flue gases

Turbulence in flue gas causes variations of the flow rate in time, which causes significant issues as the mean of that flow is rather instable. This phenomenon is illustrated in figure 28. Still according to Finnish recovery boiler committee the flue gas flow of the RB in several mills is done by computational methods. Integrating Pitot-tube may be used, but still the actual amount of the flue gas is black liquor combustion calculation averaged to the year (Jussila 2007).

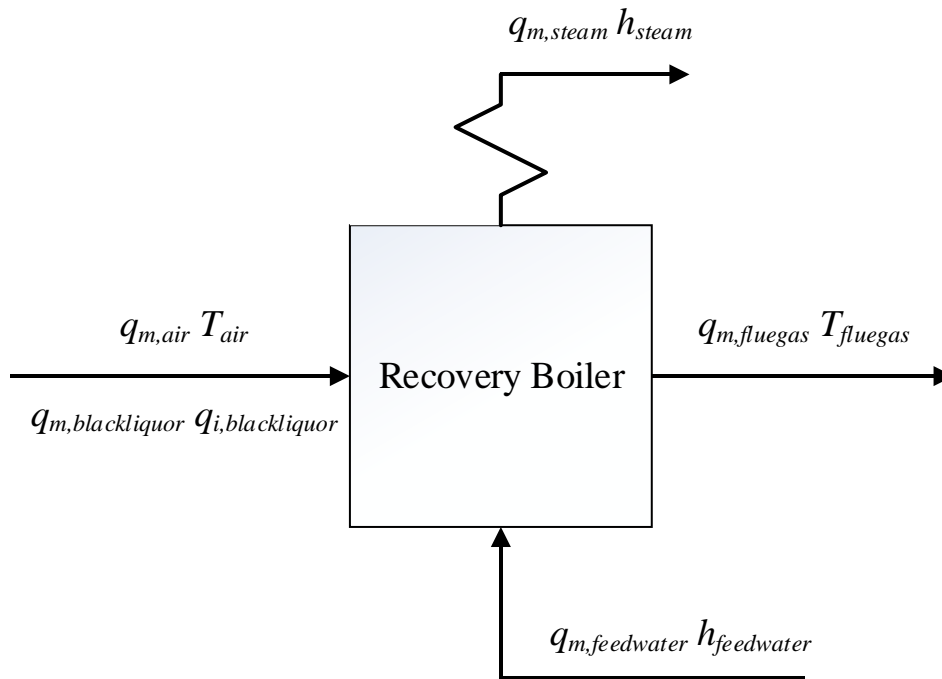


**Figure 28** RB steam and flue gas flow (hourly averages) as example of flow rate changes. The red one is the steam (kg/s) and the blue line is flue gas flow (Nm<sup>3</sup>/s) (Hamaguchi&Vakkilainen 2010, 29).

Faults may cause shut down of a boiler, start up and failure of measuring device or calibration cause changes in flue gas flow. Higher flue gas flow – higher steam flow is noticeable. Flue gas flow is reported in form of Nm<sup>3</sup>/s. Figure 28 is adopted from hourly data from a Finnish mill for a year. Depending on how a mill is run throughout the year, these values differ.

### 4.3.2 Indirect method for combustion gas flow, through mass flow of the fuel

Indirect method is available by making a mass balance for the fuel. Principle of what goes in as the black liquor fuel and feed water and what goes out is flue gas and heated steam. Figure 29 demonstrates the energy – and mass balance of these fluid flows.



**Figure 29** RB power – and mass balance. (Hammo 2000, 6)

Energy balance is

$$q_{m,steam}\Delta h = \sum_i (q_{m,i}q_{black\ liquor,i}) - q_{m,flue\ gas} \int c_p dT \quad (5)$$

where

$q_{m,steam}\Delta h$  is boilers net power

$\sum(q_{m,i}q_{black\ liquor,i})$  is total fuel power (=mass flow \* heating value)

$q_{m,flue\ gas} \int c_p dT$  is flue gas loss



Additionally RB might combust concentrated non-condensable gas (CNCG). Many mills handle their CNCG in RB to convert smelly compounds to simpler ones to prevent odor problems. Weak gases or diluted non-condensable gases (DNCG) can also be destructed in the RB.

#### 4.3.3 Emissions relation to stack gas flow rate in observed period of time

Emissions are usually reported in form of ppm in stationary stack gas flows. Parts per million ppm is usually determined in volumetric proportion and for PM mass to volume is common, mg/m<sup>3</sup>n.

When reporting the annual total mass of a compound, which were discharged into the atmosphere, the actual averaged annual flow rate must be obtained. Compounds that would be given as volumetric part or mass-to-volume are NO<sub>2</sub>, NO, SO<sub>2</sub>, SO<sub>3</sub>, sulphuric acid aerosols, methyl mercaptans, H<sub>2</sub>S, CO<sub>2</sub>, C<sub>x</sub>H<sub>y</sub>, CO, H<sub>2</sub>O, O<sub>2</sub>, N<sub>2</sub>, ash, heavy metals, gaseous chlorides HCL – equivalents, Hg, NH<sub>3</sub>, Gaseous fluorides HF–equivalents, VOC, total gaseous organic carbon TVOC, PCDDs/PCDFs and dioxin-like PCBs (JRC 2017, 34).

$$m(t)_i = V(\dot{t}) \times C_i(t)dt \quad (6)$$

where  $m_i$  is compound mass over the time period  
 $V$  is volumetric flow rate  
 $C_i(t)$  is concentration over the time  
 $dt$  differential time rate

As said in equation 6 concentration is depending on time period and volumetric time is as well time-dependent.

#### 4.3.4 Working area and the preparation for work

Measurement space is the area, where the measurement is done. As an example, an elevator lifts the measuring personnel with equipment to the right level. Needed labor aiding things other than instruments for measurement are sufficient electricity supply, dry compressed air, appropriate temperature, a weather guard, clean room, link size and placing, backspace due to longer probe and all of the needed links for successful work. Best working area for practicing is a measurement booth. It will be next to the stack and closed environment from the other installations of the mill.

Before actual emission component concentrations tests, should certain other values be pre-determined. Pressure, temperature, flow metering, particulate measurement, gaseous components are some of those values to be predetermined. Filtering, drying of the sample and amount detection are done.

#### 4.3.5 Tables of measurement technologies for compounds

In table 14 is collected name of the analytical method and its component to be metered. Some of the methods work in continuous and some in batch. Table 13 presents-certain type of methods of testing different gas components. IR is infrared and UV ultraviolet light. Industry is using in continuous metering a multicomponent gas measurer nowadays as there has been a great leap in development such devise in recent years.

**Table 13** Common measurement techniques/methods. (Aumala 2000, 325).

Measurement	technique	method	technique
O <sub>2</sub>	zirconia probe	paramagnetism	
CO	IR	catalytic oxidation	
CO <sub>2</sub>	IR		
SO <sub>2</sub>	IR	UV	UV-fluorescence
NO <sub>x</sub> (=NO <sub>2</sub> +NO)	IR	UV	chemiluminescence
particle emissions	Optical (filament lamp)	Optical (laser)	piezoelectric sensor

**Table 14** Measurement analytical method and targeted component.

Analytical principles	Target component	Continuous or batch	Remarks
Non-Dispersive Infrared (NDIR) absorption detection	CO, CO <sub>2</sub>	Continuous	
	NO	Continuous	
	N <sub>2</sub> O	Continuous	
	HC	Continuous	As "n-C <sub>6</sub> H <sub>14</sub> equivalent"
Flame ionization detection (FID)	Total hydrocarbons	Continuous	
	CH <sub>4</sub> , Non-Methane Hydrocarbons (NMHC)	Continuous or batch	In combination with NMC or GC
Chemiluminescence Detection	NO, NO <sub>2</sub> , NO <sub>x</sub> , (NO + NO <sub>2</sub> )	Continuous	
Non-Dispersive Ultraviolet (NDUV) detection	NO <sub>x</sub> (NO + NO <sub>2</sub> )	Continuous	
Paramagnetic Detection (PMD)	O <sub>2</sub>	Continuous	
Zirconia solid electrolyte method	O <sub>2</sub> , NO <sub>x</sub> , Air-to-fuel ratio	Continuous	In-situ measurement (non-sampling)
Fourier Transform Infrared (FTIR) spectroscopy	N <sub>2</sub> O NH <sub>3</sub> CO, CO <sub>2</sub> , NO, H <sub>2</sub> O, NO <sub>2</sub> , C <sub>2</sub> H <sub>5</sub> OH, HCHO, CH <sub>4</sub> , et cetera	Continuous	Simultaneous, multicomponent analysis
Quantum Cascade Laser Infrared (QCL-IR) Spectroscopy	NO, NO <sub>2</sub> , N <sub>2</sub> O, NH <sub>3</sub>	Continuous	Simultaneous, multicomponent analysis
Gas Chromatography	Hydrocarbons or methane	Batch	
	Alcohols	Batch	
	N <sub>2</sub> O	Batch	
High Performance Liquid Chromatography	Carbonyl compounds (HCHO, et cetera)	Batch	

All of these in table 14 presented analytical methods to work and calibrated right need in Subsection 4.3.4 mentioned preparatory determinations or information. In table 15 is similarly shown gas component, purpose for metering and necessity according to Aumala (2000).

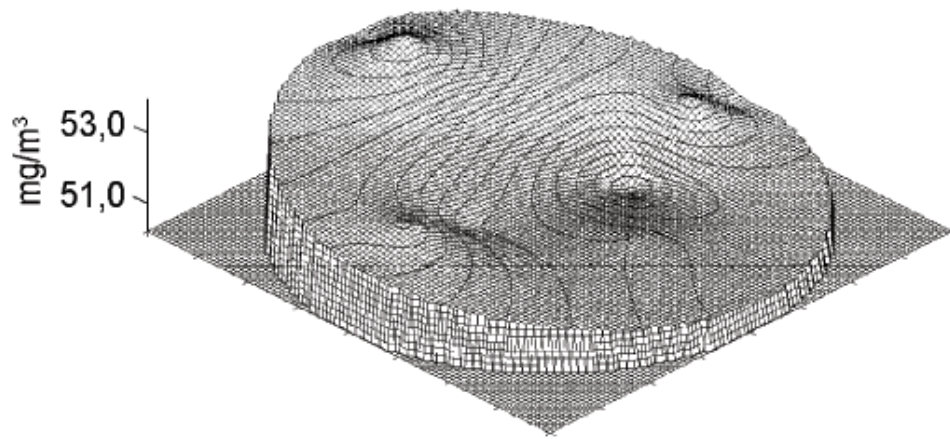
**Table 15** Flue gas components (Aumala 2000, 323).

<b>Gas component</b>	<b>Purpose of measurement</b>	<b>Measuring necessity</b>
O <sub>2</sub>	control	continuous
CO	control, emission	continuous
CO <sub>2</sub>	control, emission	continuous
SO <sub>2</sub>	control, emission	continuous/ temporary
NO (=NO <sub>2</sub> +NO)	emission	continuous/ temporary
H <sub>2</sub> S	emission	continuous/ temporary
particle emissions	emission	continuous/ temporary
heavy metals	emission	continuous/ temporary

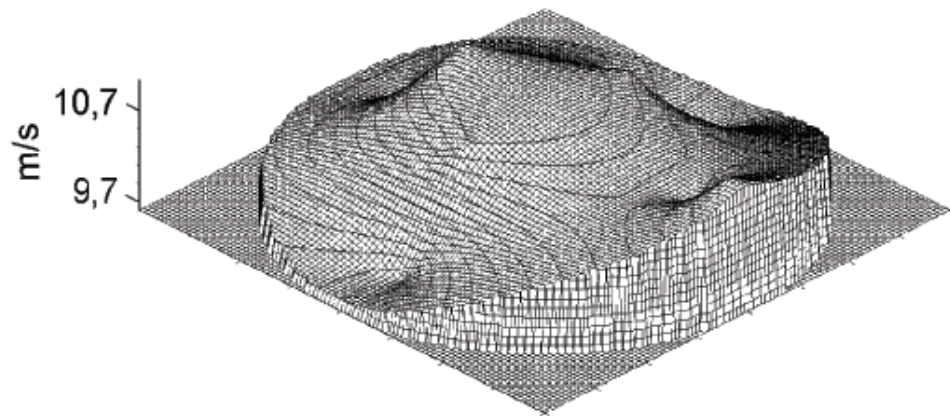
#### 4.3.6 Flow profile

Flow measurement needs to be symmetrical to calculate the real value exact. Symmetrical flow means there is certain symmetry in the gaseous flow in the pipe. Waste gas profiles are better to be homogenous than inhomogeneous. Figure 30 presents a homogenous flow profile for organic gaseous substance in a measurement plane and figure 31 presents inhomogeneous flow profiles in terms of mass concentration, velocity and mass flow density (SFS-EN 15259 2007, 71 -72).

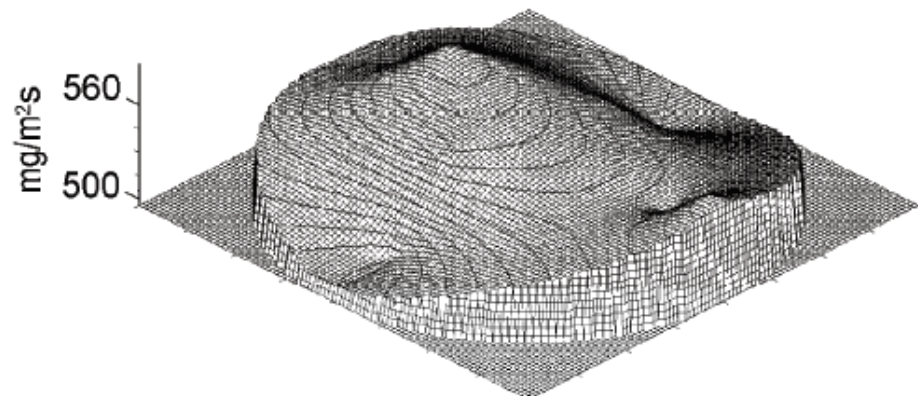
As seen in figure 30 velocities are very different in other side of the channel than other. Mills environmental staff often calculates or estimates flows and the direct measurement is not an option due to this. In Section 4.2 shortly described one optional mass flow meter, one should still remember the possibility of an inhomogeneous flow profile.



Mass concentration

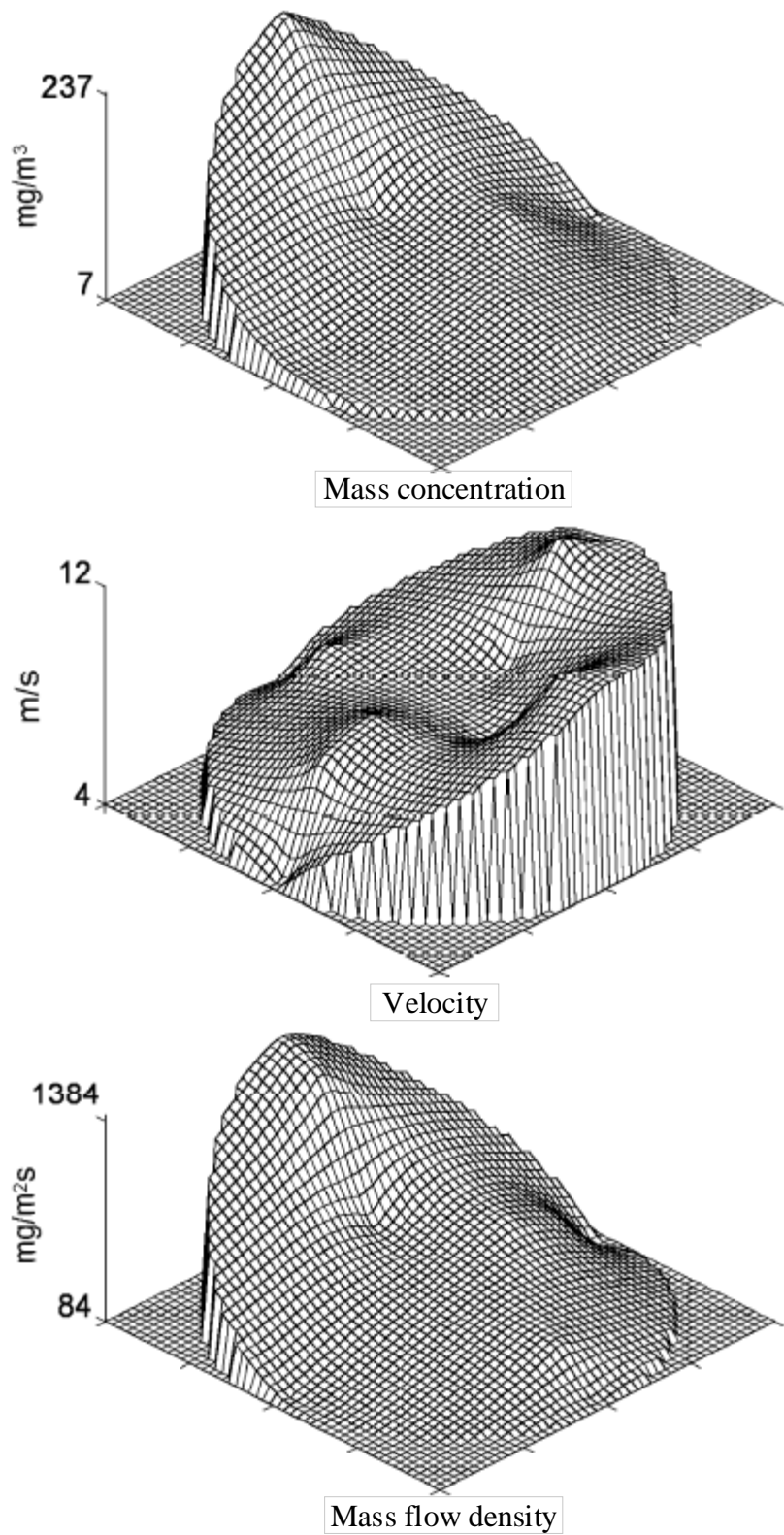


Velocity



Mass flow density

**Figure 30** Example of one component (organic gaseous substance, propane) and its homogenous measurement plane



**Figure 31** Example of inhomogeneous flow profile of organic gaseous substance (SFS-EN 15259 2007, 72)

## 5 RESULTS

As in 2018, there are 16 recovery operational boilers in Finland. We examine balances to year 2016 when there were 16 in operation. Data was given for research purposes from all of 16 operating boilers (EIPPCB 2008). Two mills have two separate RBs, so 14 columns of boilers at the tables below.

Sheet for every boiler was created and results are presented in following the sections (an example of calculation in Appendix II).

### 5.1 RBs in Finland – data

Table 16 presents the year 2016 emissions in mass. Annual emitted masses of NO<sub>x</sub>, ash and SO<sub>2</sub> are obtained statistically. Pulp production total emissions are direct air emissions. Energy production emissions are not from RB. Mass of NO<sub>x</sub> emissions are the largest in every mill compared with TRS, SO<sub>2</sub> or PM masses.

In table 17 are presented years 2016 produced pulp in tons and respect to that modelled value of specific NO<sub>x</sub> emission. For computing is used produced mass of pulp, which should not be muddled with the capacity of pulp production a given year. Lime kiln specific emissions and odour gas flare specific emissions were from 2008, while newer information was not available. It is assumed as a good estimate for year 2016 for the matter of the purpose. In table 17, for the year 2016 calculated specific emission for NO<sub>x</sub> has some deviation to reported value from the year 2008. Following in table 18 the modelled flue gas flows. The calculation example for hardwood and softwood is in Appendix II. In table 18 point %-of wood used is presumptively to be a mass percent. Process oxygen in the model is 3 % and reference oxygen content is 6 %. Comparable flue gas flows are in the last column for every RB. Mills using hardwood have smaller flue gas flows than fully, only softwood using mills. The yield chosen for the mill changes the result greatly. NO<sub>x</sub> concentration and specific emission is used as a helping parameter in these results, as it can be used as an estimating tool for the flue gas flow (table 10).

Table 19 is the flue gas table where we can see certain differences. Mill G and L have significantly smaller flow per ton than the model of combustion delivered. Also Mill C, E and M results in 400 – 600 Nm<sup>3</sup> difference with regard to modelled values. Reason for significant difference between modelled and reported flue gas flow needs to be questioned from the mills personnel. The difference might be, that the model of combustion needs RB specific changes.



**Table 16** Every Mills direct air emissions and energy production emissions. (Finnish Forest Industries 2017)

Pulp mills emissions to the atmosphere	Direct air emissions				Energy production emissions		
	SO <sub>2</sub> , t(SO <sub>2</sub> )	TRS, t(S)	NO <sub>x</sub> , t(NO <sub>2</sub> )	Particulates, t	SO <sub>2</sub> , t(SO <sub>2</sub> )	NO <sub>x</sub> , t(NO <sub>2</sub> )	Particulates, t
Mill A	37,2	5,0	181,0	14,5			
Mill B	101,6	9,3	848,7	127,4		2,2	
Mill C	136,7	34,2	1 039,2	142,9	0,3	93,6	1,3
Mill D	73,2	4,1	870,6	120,2			
Mill E	280,0	5,6	942,0	383,0			
Mill F	7,5	33,7	782,0	370,0	19,0	224,0	28,0
Mill G	60,0	17,0	1 651,0	141,0	56,0	434,0	2,0
Mill H	17,4	7,6	753,0	69,4	336,3	588,0	5,5
Mill I	26,5	6,3	633,8	341,6	13,8	93,8	2,6
Mill J	193,0	27,0	347,0	99,0	139,0	274,0	8,4
Mill K	10,2	69,3	554,5	132,4	338,0	487,7	3,5
Mill L	186,0	33,0	985,0	81,0		2,0	
Mill M	8,1	8,4	1 206,0	68,8	49,6	225,0	1,5
Mill N	43,0	30,0	1 162,0	114,0			

**Table 17** Produced pulp in tons and respect to mentioned annual NOx emissions. year of 2016.

mills with RB/RBs	produced pulp in tons ADt	Chemical pulp NOx	Lime kiln NOx*	Odor gases flare NOx*	Recovery boiler NOx *	<b>Reported for RB</b> kg/ADt
		kg/ADt	kg/ADt	kg/ADt	kg/ADt	
Mill A	<b>200 000</b>	0,91			<b>0,91</b>	<b>1,75</b>
Mill B	<b>618 700</b>	1,37	0,21		<b>1,16</b>	<b>1,22</b>
Mill C	<b>603 524</b>	1,72	0,23		<b>1,49</b>	<b>1,85</b>
Mill D	<b>585 187</b>	1,49	0,27		<b>1,22</b>	<b>1,42</b>
Mill E	<b>509 962</b>	1,85	0,36	0,050	<b>1,44</b>	<b>1,20</b>
Mill F	<b>460 000</b>	1,70	0,14	0,200	<b>1,36</b>	<b>1,13</b>
Mill G*	<b>1 126 000</b>	1,47	0,13	0,100	<b>1,24</b>	<b>1,26</b>
Mill H	<b>349 000</b>	2,16	0,34		<b>1,82</b>	<b>1,35</b>
Mill I*	<b>371 000</b>	1,71	0,24	0,040	<b>1,43</b>	<b>1,58</b>
Mill J	<b>305 000</b>	1,14	0,52		<b>0,62</b>	<b>1,63</b>
Mill K	<b>429 000</b>	1,29	0,19		<b>1,10</b>	<b>2,01</b>
Mill L	<b>655 000</b>	1,50	0,33	0,220	<b>0,95</b>	<b>1,36</b>
Mill M	<b>775 000</b>	1,56	0,05	0,180	<b>1,33</b>	<b>1,43</b>
Mill N	<b>782 000</b>	1,49	0,05	0,001	<b>1,43</b>	<b>1,05</b>

\*two RBs in mill

\*2008 questionnaire  
EIPPC\*2008  
questionnaire  
EIPPC\*2008 questionnaire EIPPC ( BREF  
Data)  
without limekiln and odorous gas flare

**Table 18** Model of combustion for every mill and flows per time and flows per pulp ton. Grey means those mills not using hardwood.

	% - of wood used		softwood					hardwood					m <sup>3</sup> n/Adt
	softwood	hardwood	m <sup>3</sup> n/Adt*	%	m <sup>3</sup> n/Adt	m <sup>3</sup> n/s	m <sup>3</sup> n/s	m <sup>3</sup> n/Adt	%	m <sup>3</sup> n/ADt	m <sup>3</sup> n/s	m <sup>3</sup> n/s	
			wet process	O <sub>2</sub> Yield used*	dry 6% O <sub>2</sub> wet, [process 3% O <sub>2</sub> dry, [process 3% O <sub>2</sub> ]			wet real O <sub>2</sub>	Yield used dry 6% O <sub>2</sub> wet, [O <sub>2</sub> -content]	dry, [process 3% O <sub>2</sub> ]			
Mill A	<b>100</b>	<b>0</b>	7 768	46	8 236	51	45	-	-	-	-	-	<b>8 236</b>
Mill B	<b>100</b>	<b>0</b>		43	9 114	174	153	-	-	-	-	-	<b>9 114</b>
Mill C	<b>65</b>	<b>35</b>		46	8 236		91		49	6 828		34	<b>7 743</b>
Mill D	<b>100</b>	<b>0</b>	8 309	44	8 808	106	94	-	-	-	-	-	<b>8 808</b>
Mill E	<b>44</b>	<b>56</b>	8 033	45	8 515	59	52	6 706	49	6 828	62	53	<b>7 571</b>
Mill F	<b>62</b>	<b>38</b>	7 928	46	8 236	74	64	6627	49	6 828	28	24	<b>7 701</b>
Mill G	<b>45</b>	<b>55</b>	8 203	45	8 515	136	117	6 857	48	7 060	138	119	<b>7 715</b>
Mill H	<b>100</b>	<b>0</b>	8 014	46	8236	91	78	-	-	-	-	-	<b>8 236</b>
Mill I	<b>100</b>	<b>0</b>	8 309	44	8 808	101	89	-	-	-	-	-	<b>8 808</b>
Mill J	<b>60</b>	<b>40</b>	8 151	45	8 515	48,63	42	7 043	47	7 301	28	24	<b>8 030</b>
Mill K	<b>35</b>	<b>65</b>	8 309	44	8 808	41	36	6 996	47	7 301	64	55	<b>7 829</b>
Mill L	<b>60</b>	<b>40</b>	7 640	46,5	8 101	98	86	6 521	49	6 828	56	49	<b>7 592</b>
Mill M	<b>38</b>	<b>62</b>	7 768	46	8 236	75	66	6 442	49	6 828	101	89	<b>7 363</b>
Mill N	<b>52</b>	<b>48</b>	8 552	44	9 114	113	101	7 127	46	7 553	87	77	<b>8 365</b>

\* all values are in stand. Cond. State

\*Yield from wood to dry unbleached cellulose in the model

**Table 19** Model of combustion results and reported volumetric flowrates in standard condition. The estimating conjecture was made by thesis worker.

	Model of combustion results m <sup>3</sup> /ADt dry, 6-% ref O <sub>2</sub>	<b>Reported (O<sub>2</sub>-level process dependent)</b> Volumetric flow rate Nm <sup>3</sup> /ADt, stand. cond., dry gas	<b>Converted to the same ref. O<sub>2</sub>-level from reported</b> Volumetric flow rate Nm <sup>3</sup> /ADt, stand. cond., dry gas (6%)	<b>Conjecture made by thesis worker from reported value</b> Volumetric flow rate Nm <sup>3</sup> /ADt, stand. cond., dry gas (6%)
Mill A	<b>8 236</b>	-	-	-
Mill B	<b>9 114</b>	<b>8 250</b>	<b>9 900</b>	-
Mill C	<b>7 743</b>	<b>7 356</b>	<b>7 356</b>	7 341
Mill D	<b>8 808</b>	<b>7 630</b>	<b>8 902</b>	-
Mill E	<b>7 571</b>	<b>7 128</b>	<b>7 128</b>	7 603
Mill F	<b>7 701</b>	<b>7 600</b>	<b>9 000</b>	8 610
Mill G	<b>7 715</b>	<b>5 800</b>	<b>5 800</b>	-
Mill H	<b>8 236</b>	<b>7 250</b>	<b>8 410</b>	-
Mill I*	<b>8 808</b>	<b>10 491</b>	<b>9246 / 10673</b>	10 078
Mill J	<b>8 030</b>	<b>8 069</b>	<b>8 069</b>	-
Mill K	<b>7 829</b>	<b>7 600</b>	<b>8 107</b>	-
Mill L	<b>7 592</b>	<b>6 800</b>	<b>6 845</b>	7 782
Mill M	<b>7 363</b>	<b>6 642</b>	<b>6 775</b>	7 730
Mill N	<b>8 365</b>	<b>7 400</b>	<b>8 387</b>	-

\* reported values for two different RBs

\*combined for both RBs

**Table 20** Total flow per second and modelled flows to specific emissions, which results concentration of NO<sub>x</sub>.

	Model of combustion flow and NO <sub>x</sub> concentrations		Modelled Nm <sup>3</sup> /ADt to reported kg/ADt Nox (2008)
	m <sup>3</sup> n/s	mg NO <sub>2</sub> /m <sup>3</sup> n ( kg/ADt 2016)	mg NO <sub>2</sub> /m <sup>3</sup> n
	dry, process 3 % O <sub>2</sub>	dry, 6% ref O <sub>2</sub>	dry, 6% ref O <sub>2</sub>
Mill A	<b>45</b>	110	-
Mill B	<b>153</b>	127	<b>134</b>
Mill C	<b>125</b>	193	<b>239</b>
Mill D	<b>94</b>	138	<b>161</b>
Mill E	<b>105</b>	190	<b>159</b>
Mill F	<b>88</b>	177	<b>147</b>
Mill G	<b>236</b>	161	<b>163</b>
Mill H	<b>78</b>	221	<b>164</b>
Mill I	<b>89</b>	162	<b>179</b>
Mill J	<b>67</b>	77	<b>203</b>
Mill K	<b>91</b>	141	<b>257</b>
Mill L	<b>135</b>	126	<b>179</b>
Mill M	<b>155</b>	180	<b>194</b>
Mill N	<b>178</b>	172	<b>126</b>

**Table 21** A study of reported values to year 2016 or either to year 2008. Oxygen content was noticed to be inconsistent in reporting in EIPPC 2008.

	Reported flue gas to 2016 NOx kg/(ADt) mg NO <sub>2</sub> /m <sup>3</sup> n dry, 6% ref O <sub>2</sub>	Reported flue gas to reported Nox (2008) mg NO <sub>2</sub> /m <sup>3</sup> n dry, 6% ref O <sub>2</sub>	Conjecture flue gas to 2016 NOx kg/ADt mg NO <sub>2</sub> /m <sup>3</sup> n dry, 6% ref O <sub>2</sub>	Conjecture and reported 2008 mg NO <sub>2</sub> /m <sup>3</sup> n dry, 6% ref O <sub>2</sub>	<b>Reported EIPPC concentration</b> mg NO <sub>2</sub> /m <sup>3</sup> n dry, O <sub>2</sub> varying reported differently	<b>Reported</b> mg NO <sub>2</sub> /m <sup>3</sup> n dry, 6% ref O <sub>2</sub>
Mill A						
Mill B	117	123			162	162
Mill C	203	251	203	252	252	252
Mill D	137	160			165	142
Mill E	202	168	189	158	171	171
Mill F	151	126	158	131	140	131
Mill G	214	217			220	220
Mill H	216	161			170	170
Mill I	142	157	142	157	156	156
Mill J	77	202			202	202
Mill K	136	248			236	236
Mill L	139	198	123	175	175	175
Mill M	196	211	172	185	185	185
Mill N	171	125			124	124

Table 20 is models off-gas and specific NO<sub>x</sub> emission per tonne turned to average annual concentration. The specific emissions are from the table 17. Flows are in dry condition, even in reality off-gas is always wet and not dry.

Table 21 presents reported NO<sub>x</sub> concentrations, differences are to be examined.

Conjecture from reported values is done by changing some of the values by the thesis worker. Conjecture utilizes EIPPC reports and looks at them mathematically by the help of general principles presented in table 10. EIPPC are not publicly published. Conjecture also includes one mills that gave corrected flue gas amounts privately to the thesis worker. Those values follow better the general trend and thesis worker self believes they correlate better. Conjecture values were set for help of understanding and check.

## 5.2 Other reported volumetric flows of some RBs

Reported values for flue gas flow for RB are two different sets one was obtained from BREF PP 2015 that should have been the same as in EIPPCB questionnaires. In table 22 some of the Finnish mill locations names and the publically reported volumetric flue gas flows.

**Table 22** BREF page 304 year 2007/2009

	Nm <sup>3</sup> / ADt	
Joutseno	9 900	
Kemi	7 356	
Rauma	8 902	
Äänekoski	7 603	
Oulu	8 410	
Sunila SE 1	3 840	sum for two
Sunila SE 2	6 214	10 054
Varkaus	5 069	
Veitsiluoto	8 107	
Kaukas	6 845	
Pietarsaari	8 387	

Variety in flows is due to utilization rate of hardwood. The larger the off-gas flow, the more likely hardwood is used as raw material in table 22.

### 5.3 Typical wood consumption rate to produced pulp

Wood consumption is an interesting factor as we examine mills performance. Cellulose is only a part of the wood. Table 23 shows examples of wood utilization rates, the source is not mentioned due to the context of the thesis.

**Table 23** Mills B, C, D and E information of wood consumption related to produced pulp (2016)

	<b>Mill B</b>	<b>Mill C</b>	<b>Mill D</b>	<b>Mill E</b>
<b>tons of pulp</b>	618 700	603 524	585 187	509 962
<b>total wood consumption 1000 m<sup>3</sup></b>	3 406	3 061	3 211	2 336
<b>wood per pulp m<sup>3</sup>/t</b>	5,5051	5,0719	5,4871	4,5807
<b>pulp per wood t/m<sup>3</sup></b>	0,1817	0,1972	0,1822	0,2183

Mill B and Mill D are fully softwood operating mills and Mill C and E use partly hardwood. Mill B needs more wood than Mill D and reports higher off-gas volume (table 19). Mill E has a higher %-consumed hardwood rate than Mill C (table 18). Both mills B and D have higher reported and modelled flue gas amount than mills C and E.

UPM reports on its annual report (2016) that typical average in mills is 4,44 m<sup>3</sup>/t of produced pulp for all of its chemical pulp mills across the world. Eucalyptus mills need less wood for operating the same amount of pulp as it is hardwood and has a higher yield than Nordic hardwood or softwood. UPM owns eucalyptus mills.



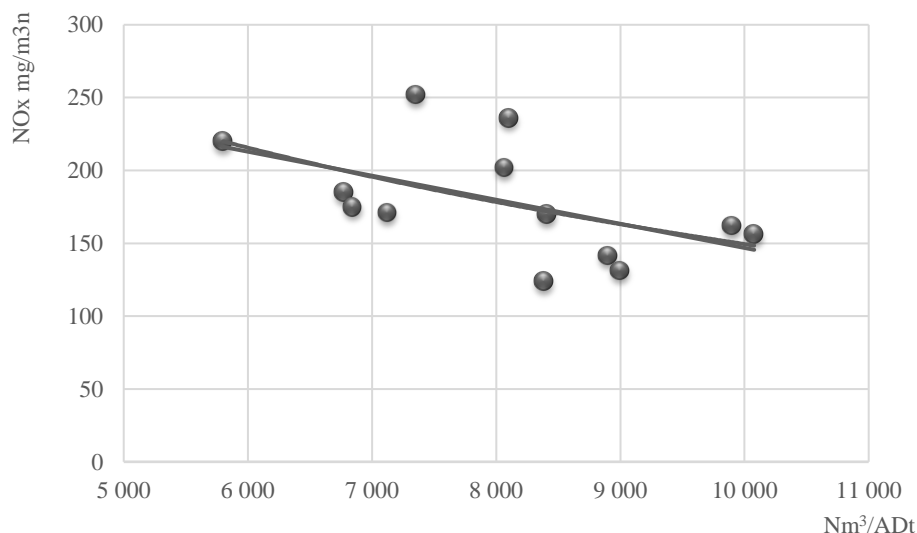
## 6 INTERPRETATION OF RESULTS

### 6.1 Flow corrections

Before making assumptions in the future, as making flue gas flow a parameter for the yield of products, should be made sure that if those reported flue gas flows are right and precise averaged yearly. Some of those reported values of the RB flue gas flow even after changing to reference oxygen levels are higher or lower than expected from the model of combustion and differences between mills were obtained. In the model of combustion or through NO<sub>x</sub> emission calculation made possible to get flows that are different than reported ones. The methods and possibilities of the thesis work did not make possible to have the full sureness of the flow from a certain pulp mills RB.

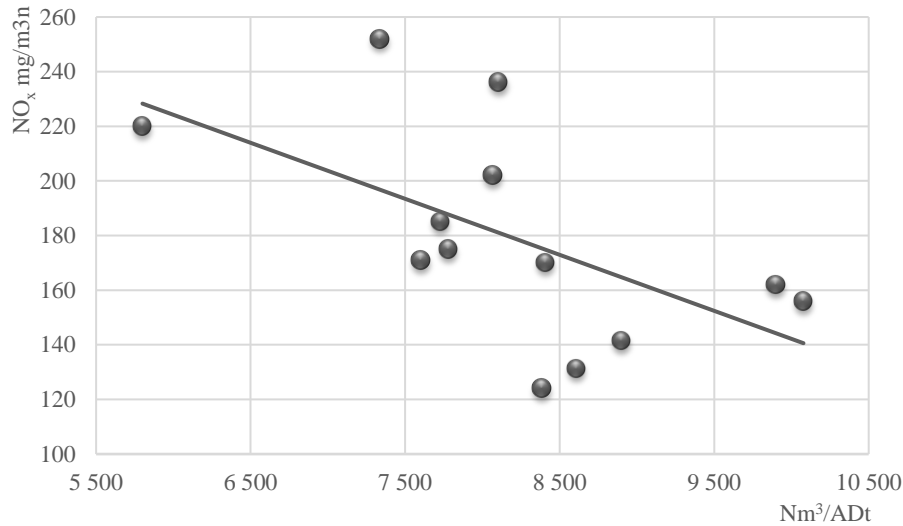
### 6.2 NO<sub>x</sub> concentration to off-gas volumetric flow

If lower NO<sub>x</sub> concentration is due to a larger volume of off-gas (in the reference state), the environmental benefit of reducing NO<sub>x</sub> concentration is not very beneficial. Figure 32 has some inclination. Every ball presents a pulp mill.



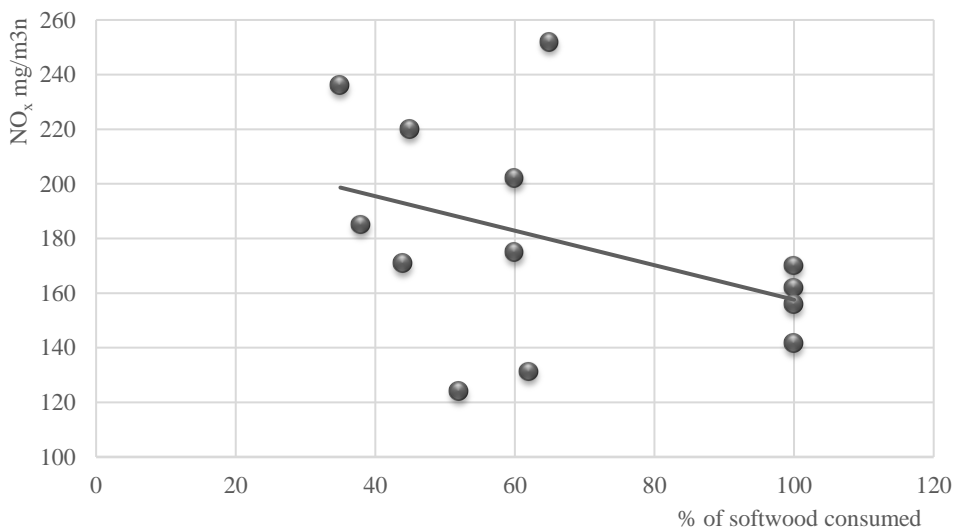
**Figure 32** Reported flows and reported NO<sub>x</sub> concentration [mg/m<sup>3</sup>n]. Trend line presents reported values NO<sub>x</sub> concentration declines as volume grows [Nm<sup>3</sup>/ADt]

Assumptions on, if Nordic hardwood produces higher  $\text{NO}_x$  concentration annual average than softwood is less correlating, but a remarkable trend is to be found. Modelled concentrations and modelled flue gas flow have lesser correlation.



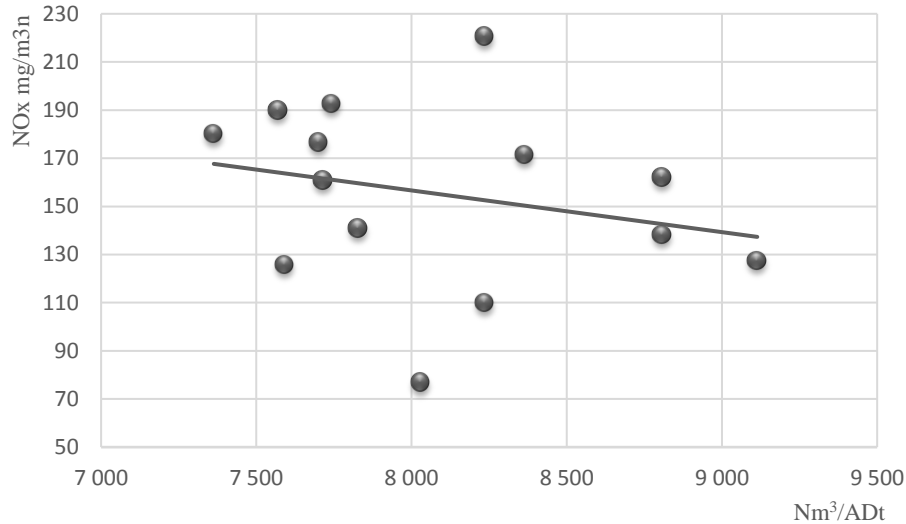
**Figure 33** Conjecture flue gas to  $\text{NO}_x$  concentration reported in EIPPC (2008).

Figure 33 presents thesis workers conjecture off-gas volume to reported  $\text{NO}_x$  concentration ( $\text{mg}/\text{m}^3\text{n}$ ), drawn values are from table 19. As flue gases are more, the trend is that  $\text{NO}_x$  concentration level in it lowers. In figure 34 seemingly also for hardwood mills  $\text{NO}_x$  can be more.



**Figure 34** Reported  $\text{NO}_x$  and hardwood correlate less, but the trend is down.

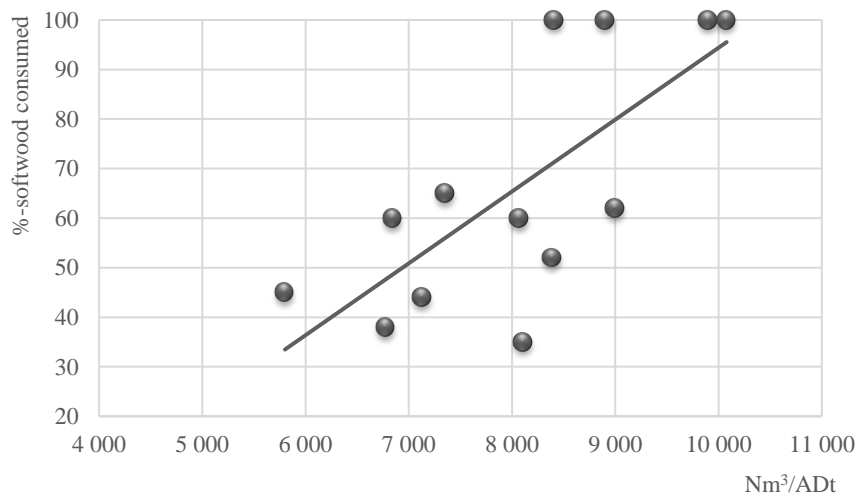
The model of combustion and its  $\text{NO}_x$  concentration was created. In figure 35 shows resulting trend line for modelled values for year 2016.



**Figure 35** Model of combustion and  $\text{NO}_x$  ( $\text{mg}/\text{m}^3\text{n}$ ) 2016 to flue gas modelled.

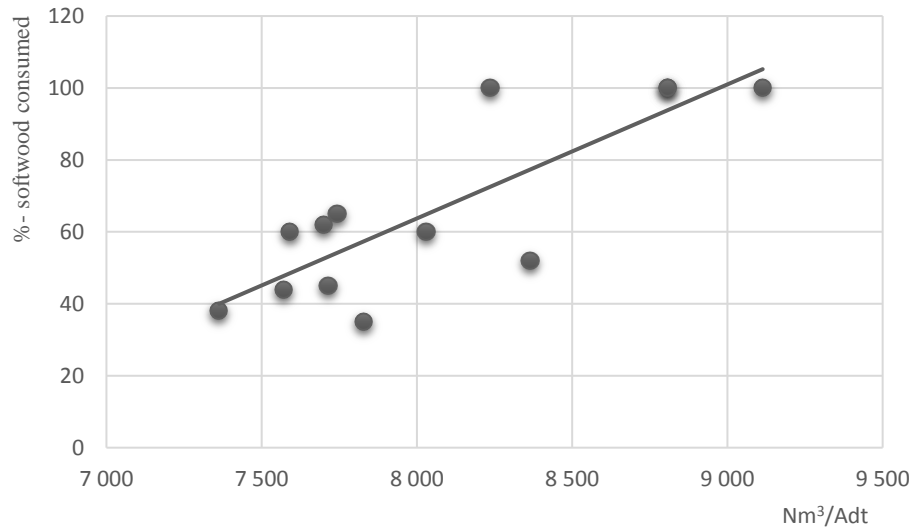
### 6.3 Exit gas volume to softwood proportion

Reported flue gas flows in right reference oxygen are presented in this section. Figure 36 presents flue gas to its softwood proportion in the year 2008, higher flue gas amount higher softwood usage.



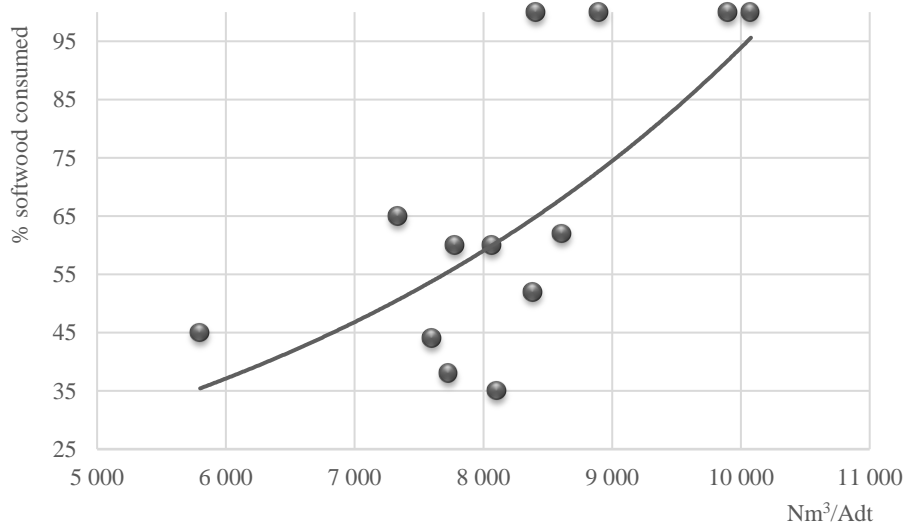
**Figure 36** Reported flue gas flow to %- softwood consumed (reported year 2008).

Figure 37 presents well that model of combustion result and exit gas raise along. Many of Chapter 6 presented figures are best to be presented as linear, also logarithmic trend line, exponential trend lines were tested for each figures, if they show any changes.



**Figure 37** Model of combustion flue gas volume and reported softwood-% consumed

Lastly conjecture, with small changes to reported flue gas flows is presented in figure 38. Here is exponential trend line used. Conjecture for flue gas flow is from table 19.

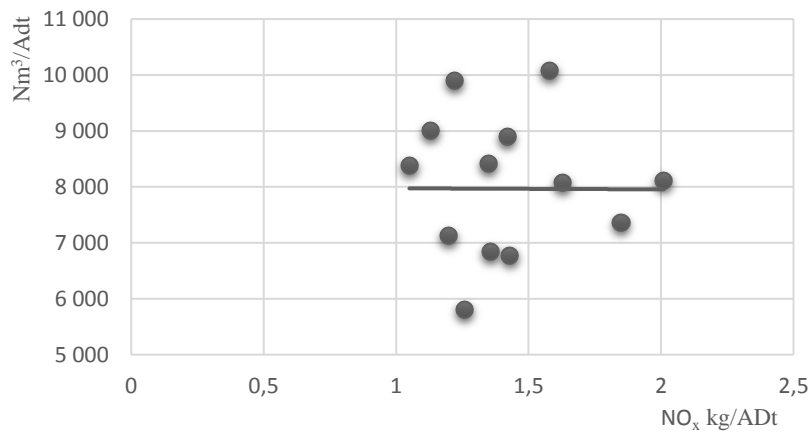


**Figure 38** Conjecture Nm³/ADt and softwood content [%]

Flue gas flow rate from RB could estimate how much of incoming roundwood is left to solid or liquid products and what proportion is becoming gaseous off-gas.

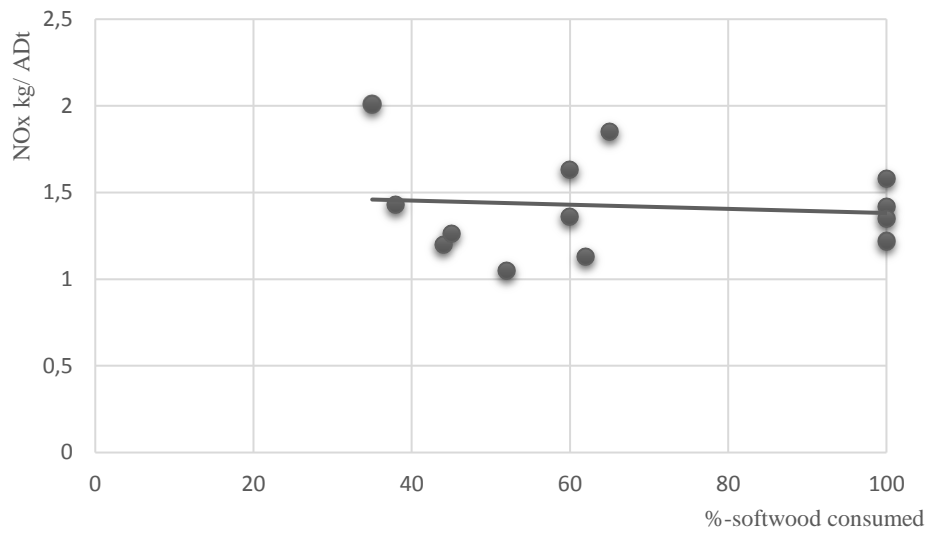
## 6.4 Specific emissions

Reported specific emissions for  $\text{NO}_x$  does not depend from flue gas amount seemingly, in figure 39.



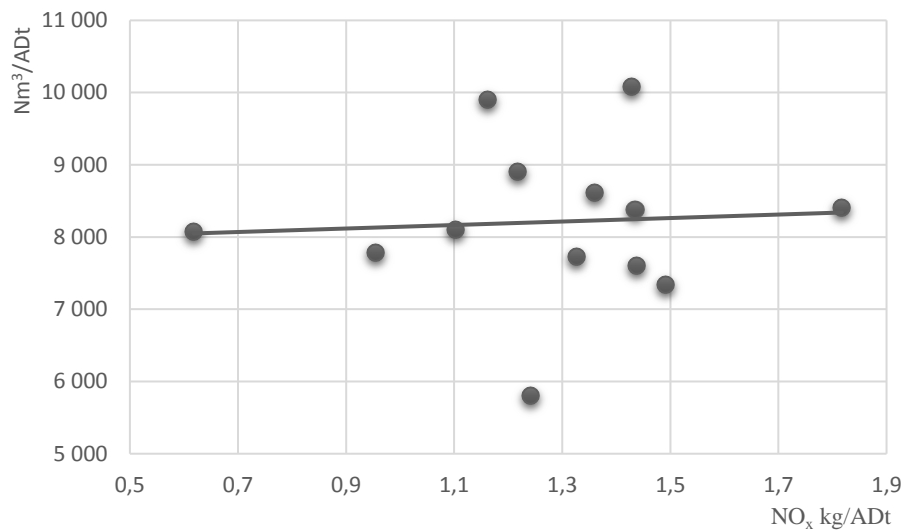
**Figure 39** Reported volume  $\text{Nm}^3$  to  $\text{kg/ADt NO}_x$  year 2008.

Both big and small volume of RB's flue gas produces higher or smaller specific emission of  $\text{NO}_x$ . Hardwood proportion in reported values show larger variety in  $\text{kg NO}_x/\text{ADt}$  than only softwood using pulp mills, in figure 40.

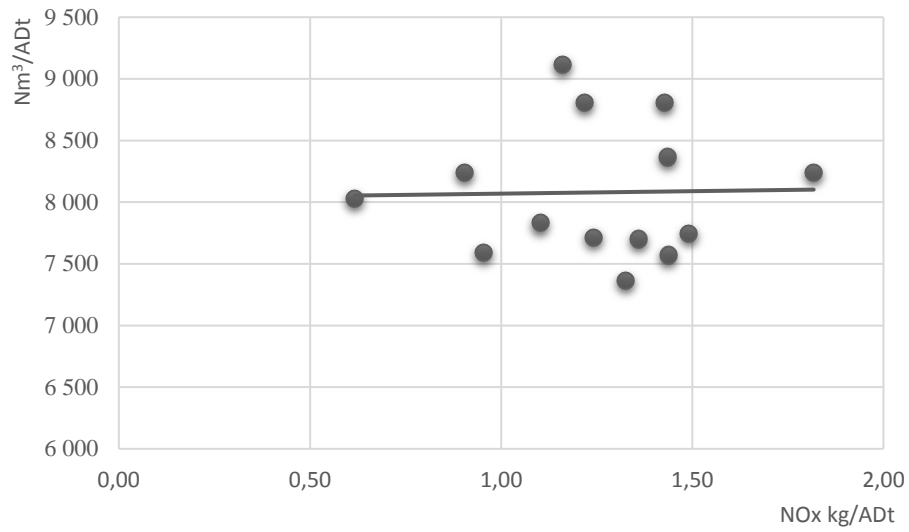


**Figure 40** Reported NO<sub>x</sub> kg/ADt and softwood consumed % year 2008.

The conjecture off-gas volume made by thesis worker from reported values and years 2016 approximated specific NO<sub>x</sub> emissions present no sharp angle in trend line, in figure 41.



**Figure 41** Conjecture volume of flue gas and 2016 NO<sub>x</sub> specific emission in kg/ADt.



**Figure 42** Modelled flue gas volume Nm<sup>3</sup>/ADt and recovery boiler NO<sub>x</sub> (kg/ADt) in year 2016.

Specific NO<sub>x</sub> per produced ton of pulp generate no changes from gas volumetric or hardwood consumption rates.

## 7 CONCLUSIONS

Fluid movement in a channel of the RB furnace is needed to make balances for other emissions. Reporting of values there should be oxygen content clearly presented. For the balances to be plain, must be an implementing rule for giving the flue gas flows, in the same gas state. Also notification to water content and other certain parametric measurements (pressure and temperature), a simultaneous time frame for every parameter is needed for qualified flue gas flow results. Reference oxygen content for air emissions from the RBs in Finland is 6%. (Pellikka 2018)

Pulp mills have differences on their operation and flue gas amount that they produce into the surrounding atmosphere. Wood specie influences the flue gas flow. Hardwood produces less flue gas per ton of pulp as it has different chemical composition (Hakkila&Verkasalo 2009, 147). Open policy on why some mills at least report the lower exit gas flows than other, which indicates higher yield of pulp, could help the overall industry to set better operation possibly in the future.

The Best Available Techniques Reference Document for the Production of Pulp, Paper and Board (2015) page 795 does not greatly differentiate between hardwood and softwood the concentration of NO<sub>x</sub>. NO<sub>x</sub> concentration tend to be higher than 200 mg/m<sup>3</sup>n in some mills operating hardwood due to higher yield and lower off-gas volume. Specific emission levels (kg NO<sub>x</sub>/ADt) are more to be observed in the RBs for comparison. Generally, some of the pulp mills operate at very high dry solids content of black liquor and a higher yield of pulp from wood, which is good for many reasons, but results in higher NO<sub>x</sub> concentrations in the off-gas.

One finding is that if the higher volume of flue gas per tonne of produced pulp – means that more material was released into the atmosphere and not utilized as a bio-based product. The same atoms, where combusted to the air as these atoms had not been transmuted to useful chemical pulp or a by-product. Energy recovery from black liquor is a common method in a pulp mill and remains, because of the importance for running the factory well.



In Section 3.2, Subsection 3.2.1, Subsection 3.2.2, Subsection 3.2.3 and Subsection 3.2.4 given thoughts and ideas on influencing factors affecting flue gas amount was not possibly to be numerically studied, while this information as the yield of pulp, processes, boiler overload or by-product capture levels are not given. For future research perhaps would give useful information of the performance of the pulp mill, if inside every mill staff of the pulp mill would make a flue gas amount comparison to these private data.

Lignin has a prospective outlook in the future, it is turning to a product to be sold to the chemical industry makes it valuable to customers, it might be that RBs work in the future only for self-sufficiency reasons and process improvements (Bajpai 2010). Lignin markets still need to be established. Next steps in Finnish companies in coming years will be reducing the waste or reutilization of it as a by-product. Also these companies that own RBs in their pulp mill components have made great plans to find new solutions to make more profit and contributions to the environmental protection.

## 8 SUMMARY

Forest industry and its pulp mills are many, where several workers employ themselves in. RB releases air emissions, which are effected processes and wood species. Wood species are mainly two utilized in Finnish kraft pulp mills. Those wood species have different chemical composition. . Obtaining a desirable product it is important to use different wood species in pulping. Species pine, birch and spruce are the main three by total mass in Nordic countries in kraft pulp mills. The main component incinerated in RB is lignin. Softwoods have higher lignin content.

Step-by-step changes in emissions and energy balances have been used. Various purification techniques for air emissions have been adopted. Finnish kraft pulp mills saw significant reduce of sulphuric air emissions in the years 1990 – 2007 by increasing the dry solids content of the black liquor and by lime mud drying technologies.

Pulp mill contains two main lines fibre line and recovery line. We examined RBs flue gas flow, which are the largest flue gas flow from the pulp mills units. Recovery systems main tasks are inorganic pulping chemicals recovery, incineration of dissolved organic material, organic by-products capture (tall oil) and prevention and control of pollutants. Without recovery system waste water load would be higher and as well as emissions to air.

Reporting and measuring atmospheric emissions have legal binding in EU countries. Concentration and the specific pollutant are reported. Periodic and continuous measurement are different. Relevant parameters for a certain measurement component are pressure, temperature, oxygen, CO and water vapour content in flue gas for combustion processes. Simultaneous and on the same time frame reported data gives a more accurate result for others such as exit gas flow and concentration values. If there is other parameter monitored only periodically and the other continuously, mathematically considered results are not dependable enough.

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**Mill B typical information given in datasheet for measurement of recovery boiler**

<b>BLACK LIQUOR</b>	<b><u>units</u></b>
Liquor flow	tds/d
dry solids content in guns	%
density at guns	kg/l
temperature in the storage tank	°C
flow front	l/s
flow right	l/s
flow left	l/s
flow rear	l/s
<b>FW &amp; STEAM</b>	
FW	kg/s
CBD	kg/s
SB	kg/s
net steam	kg/s
<b>AUX FUEL IN OPERATION</b>	
load gas	m <sup>3</sup> n/s
start up gas	bar
load gas	bar
<b>AIR</b>	
primary left	m <sup>3</sup> n/s
primary right	m <sup>3</sup> n/s
secondary left	m <sup>3</sup> n/s
secondary right	m <sup>3</sup> n/s
load burner air	m <sup>3</sup> n/s
tertiary front	m <sup>3</sup> n/s
tertiary rear	m <sup>3</sup> n/s
Strong to combustion	m <sup>3</sup> n/s
Strong to combustion	kg/s
<b>FLUE GAS</b>	
CO left	ppm
CO right	ppm
SO <sub>2</sub>	mg/m <sup>3</sup> n
TRS	mg/m <sup>3</sup> n
NO <sub>x</sub>	mg/m <sup>3</sup> n
Dust	%
O <sub>2</sub> after BB left	%, wet
O <sub>2</sub> after BB right	%, wet

### Hardwood model for the Mill G

<b>Wood species in cooking</b>	3		<b>Composition of formed black liquor dry solids</b>				
Air dry unbleached cellulose	1745 t/24 h	355 days/y	Mill liquor	33,9 %	C	laboratory	laboratory
Yield in Oxygen delignification	95 %			3,5 %	H	33,84 %	Org acids
Yield from wood to dry unbleached cellulose	54 %	48-55		0,1 %		3,81 %	lignin
Pulp kappa before oxygen delignification	18			5,9 %	S	5,87 %	Soap
Pulp kappa after oxygen delignification	13			19,3 %	Na	23,50 %	Other org
Washing efficiency unbleached pulp	99 %			1,5 %			Org. Na
Washing efficiency bleached pulp	99 %			0,3 %			NaOH
Soap recovery efficiency	80 %			35,5 %	O	32,98 %	Na2S
Water created when wood acids are neutralized	100 kg/t Bleached pulp			26,9	SUM	67,02 %	Na2CO3
NCG generation during cook	3 % wood			41,76			Na2SO4
Sulfur in NCG	2 kg/t Bleached pulp			0,97			SUM
				4,38			100,00 %
<b>White liquor</b>			<b>Chemical composition of wood</b>				
Active alkali, Na2O-% per wood	19 %		Cellulose	40 %			
White liquor sulfidity	40 %		Hemicellulose	37 %			
White liquor dry solids	15 %		Lignin	20 %			
Causticity	80 %		Extractives	3 %			
Reduction in white liquor	95 %		<b>Summary</b>	100			
Black liquor dry solids	73 %		Wood type	hardwood			
<b>Oxidized White liquor</b>							
Oxidized White liquor used in Oxygen delignification	200 kg/t Bleached pulp						
Methanol formation in Oxygen delignification	0,2 kg/t Bleached pulp						

### Heating value of black liquor dry-solids 13834 kJ/kg BLDS

Heat in to recovery boiler	18,246 GJ/t Bleached pulp
Heat in to recovery boiler per second	0,332 GJ/s
Massflow to recovery boiler	2153,0 tDS/24h
Massflow to recovery boiler	24,9 kgDS/s

		<u>comparison</u>
<b>Organic compounds</b>	Air dry bleached pulp pulp	1657,282 t/24h
	Dry bleached pulp pulp	2850
	Dry unbleached cellulose	1492 t/24h
	Dry wood needed	2565
	Wood needed to make 1000 kg unbleached	1570 t/24h
	Loss as volatiles (including TRS-compounds)	2700
	TRS-compound loss (assumed as methylmerkaptan)	2908 t/24h
	Water generated when acids in wood are neutralized	5870
	Organic compounds in Black liquor	1852 kg/t Bleached pulp
	Organic compounds in pulp	2174
	Lignin in wood to make 1 t of unbleached pulp	56 kg/t Bleached pulp
	Lignin in unbleached pulp	65
	Lignin in Black liquor	3 kg/t Bleached pulp
	Tall oil from rosins and fatty acids	3
	Tall oil remains	100 kg/t Bleached pulp
	Tall oil recovered	100
	Tall oil in black liquor	797 kg/t Bleached pulp
	Other organic compounds formation (4 % from wood)	1110
	Other organic compounds to pulp	996 kg/t Bleached pulp
	Other organic compounds to Black liquor	370 kg/t Bleached pulp
	Organic acids to Black liquor	435
	<u>Sum of Organic compounds to Black liquor</u>	28
	Lignin heating value	342 kg/t Bleached pulp
	Rosins and fatty acids heating value	390
	Organic acids heating value	2 kg/t Bleached pulp
	Other organic compounds heating value	2
	<u>Sum of organic compounds heating value</u>	0
		74 kg/t Bleached pulp
		87
		1 kg/t Bleached pulp
		1
		73 kg/t Bleached pulp
		86
		381 kg/t Bleached pulp
		634
		797 kg/t Bleached pulp
		1110
		8597 kJ/kg Bleached pulp
		9788
		15 kJ/kg Bleached pulp
		15
		5280 kJ/kg Bleached pulp
		8597
		1390 kJ/kg Bleached pulp
		1632
		15281 kJ/kg Bleached pulp
		20031

<b>White liquor</b>	Active alkali, NaOH-% per dry wood	24 %	24
	Active alkali kg/t unbleached pulp, Na <sub>2</sub> O	352 kg/t Bleached pulp	402
	Active alkali kg/t unbleached pulp, NaOH	449 kg/t Bleached pulp	514
	NaOH charge as Na <sub>2</sub> O	211 kg/t Bleached pulp	261
	NaOH charge as NaOH	272 kg/t Bleached pulp	337
	Na <sub>2</sub> S charge as Na <sub>2</sub> O	141 kg/t Bleached pulp	141
	Na <sub>2</sub> S charge as NaOH	182 kg/t Bleached pulp	182
	Active alkali concentration, Na <sub>2</sub> O	115 g/l	112
	Active alkali concentration, NaOH	148 g/l	144
	(estimate) White liquor density	1169 g/l	1169
	Na <sub>2</sub> CO <sub>3</sub> in white liquor as Na <sub>2</sub> O	42 kg/t Bleached pulp	58
	Na <sub>2</sub> SO <sub>4</sub> in white liquor as Na <sub>2</sub> O	7 kg/t Bleached pulp	8
	<u>Sum of inorganic compounds in white liquor</u>	<u>538 kg/t Bleached pulp</u>	<u>632</u>
Sum of inorganic compounds in white liquor as Na <sub>2</sub> O	401 kg/t Bleached pulp	468	
<b>Black liquor</b>	NaOH in black liquor	50 kg/t Bleached pulp	<u>114</u>
	Organically bound Na in black liquor	129 kg/t Bleached pulp	<u>129</u>
	Na <sub>2</sub> S in black liquor	170 kg/t Bleached pulp	<u>170</u>
	Na <sub>2</sub> CO <sub>3</sub> in black liquor	71 kg/t Bleached pulp	<u>97</u>
	Na <sub>2</sub> SO <sub>4</sub> in black liquor	16 kg/t Bleached pulp	<u>19</u>
	<u>Inorganic compounds in black liquor</u>	<u>437 kg/t Bleached pulp</u>	<u>530</u>
	<u>Inorganic compounds, (Na<sub>2</sub>S heating value)</u>	<u>2199 kJ/kg Bleached pulp</u>	<u>2199</u>
<b>Inorganic compounds in wood</b>	NaOH pulp	1 kg/t Bleached pulp	<u>1</u>
	Na in pulp organically bound	1 kg/t Bleached pulp	<u>1</u>
	Na <sub>2</sub> S pulp	2 kg/t Bleached pulp	<u>2</u>
	Na <sub>2</sub> CO <sub>3</sub> pulp	1 kg/t Bleached pulp	<u>1</u>
	Na <sub>2</sub> SO <sub>4</sub> pulp	0 kg/t Bleached pulp	0
	<u>Inorganic compounds pulp</u>	<u>4 kg/t Bleached pulp</u>	<u>5</u>
	<u>Black liquor dry solids from cooking</u>	<u>1234 kg/t Bleached pulp</u>	<u>1641</u>
<b>Oxygen stage</b>	Bleached pulp formation	950 kg/t Bleached pulp	950
	Bleached pulp inorganic compounds	5 kg/t Bleached pulp	6
	Bleached pulp organic compounds	945 kg/t Bleached pulp	944
	Loss of unbleached pulp during bleaching	50 kg/t Bleached pulp	50
	Lignin in bleached pulp	21 kg/t Bleached pulp	31
	Lignin dissolved to bleaching effluent	7 kg/t Bleached pulp	14
	Metanol creation	0,2 kg/t Bleached pulp	0
	Organic acids to bleaching effluent	43 kg/t Bleached pulp	36
	<u>Organic compounds in bleaching effluent</u>	<u>50 kg/t Bleached pulp</u>	<u>50</u>

**oxidized  
White liquor**

White liquor oxidizing reaction:  $2\text{Na}_2\text{S} + 2\text{O}_2 + \text{H}_2\text{O} \Rightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaOH}$

Oxidized White liquor used in Oxygen delignification	200 kg/t Bleached pulp	200
Unoxidized White liquor dry solids	15 %	15
Unoxidized White liquor dry matter	150 kg/t WL unoxidated	150
Unoxidized White liquor water	850 kg/t WL unoxidated	850
Unoxidized White liquor Na <sub>2</sub> S-content	33 %	28
Unoxidized White liquor NaOH-content	51 %	53
Unoxidized White liquor Na <sub>2</sub> CO <sub>3</sub> -content	13 %	16
Unoxidized White liquor Na <sub>2</sub> SO <sub>4</sub> -content	3 %	3
<b>TOTAL</b>	<b>100 %</b>	<b>100</b>

White liquor oxidation reaction:  $2\text{Na}_2\text{S} + 2\text{O}_2 + \text{H}_2\text{O} \Rightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaOH}$

Na <sub>2</sub> S in one ton of unoxidized White liquor	49 kg/t WL unoxidated	42
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> in oxidation reaction	50 kg/t WL unoxidated	43
NaOH created in oxidation reaction	25 kg/t WL unoxidated	22
Water lost in oxidation reaction	6 kg/t WL unoxidated	5

NaOH in oxidized White liquor	101 kg/1021 kg WL oxidated	102
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> in oxidized White liquor	50 kg/1021 kg WL oxidated	43
Na <sub>2</sub> CO <sub>3</sub> in oxidized White liquor	20 kg/1021 kg WL oxidated	23
Na <sub>2</sub> SO <sub>4</sub> in oxidized White liquor	4 kg/1021 kg WL oxidated	5
Water in oxidized White liquor	844 kg/1021 kg WL oxidated	845
<i>Sum of oxidized White liquor</i>	<b>1020 kg</b>	<b>1017</b>

Oxygen delignification Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> oxidized fully to Na<sub>2</sub>SO<sub>4</sub>  
 $\text{Na}_2\text{S}_2\text{O}_3 + 2\text{O}_2 + 2\text{NaOH} \Rightarrow 2\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$

Oxygen delignification NaOH used to oxidize thiosulfate	25 kg/1021 kg WL oxidated	21,55
Oxygen delignification Na <sub>2</sub> SO <sub>4</sub> created in oxidizing thiosulfate	90 kg/1021 kg WL oxidated	76,49
Oxygen delignification H <sub>2</sub> O created in oxidizing thiosulfate	6 kg/1021 kg WL oxidated	4,85
<i>Sum of water and inorganics in Bleaching residue</i>	<b>1091 kg</b>	<b>1077</b>

NaOH in oxygen bleaching residue	14 kg/t Bleached pulp	15
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> in oxygen bleaching residue	0 kg/t Bleached pulp	0
Na <sub>2</sub> CO <sub>3</sub> in oxygen bleaching residue	4 kg/t Bleached pulp	4
Na <sub>2</sub> SO <sub>4</sub> in oxygen bleaching residue	17 kg/t Bleached pulp	15
<i>Sum of Inorganic compounds to bleaching effluent</i>	<b>35 kg/t Bleached pulp</b>	<b>34</b>

**Dry solids in Bleaching residue** 85 kg/t Bleached pulp 84

**Bleaching residue  
heating value**

Lignin heating value in Bleaching residue	168 kJ/kg Bleached pulp	357
Organic acids heating value in Bleaching residue	597 kJ/kg Bleached pulp	482
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> heating value in Bleaching residue	0 kJ/kg Bleached pulp	0
<b>Bleaching residue heating value yhteensä</b>	<b>765 kJ/kg Bleached pulp</b>	<b>839</b>

**Sum of Black liquor and Bleaching residue Dry solids** 1319 kg/t Bleached pulp 1725

Liquor analysis		Design value	Estimate from HHV
Flow	Tds/d	2300,8	
HHV	MJ/kgds	13,83	13,8
C	mass-%, c	33,95	33,9
H	mass-%, c	5,87	5,9
N	mass-%, c	0,10	0,1
S	mass-%, c	5,87	5,9
Na	mass-%, c	19,26	19,3
K	mass-%, c	1,50	1,5
Cl	mass-%, c	0,30	0,3
Inorganics	mass-%, c	26,9	26,9
Dry solids	%	73	73
Air ratio	-	1,164	1,164



## Wood species    Compounds in liquor and their heating values

Wood species	Compounds in liquor and their heating values	SI heating value	C %	H %	O %	Na %	S %	Muut %	yht	
Pine										
Spruce	ORG. ACIDS FROM CARBOHYDRATES									
Birch	softwood (Pine)	13855 kJ/kg	46	6	48	0	0	0	100	
Euca	softwood (Spruce)	13340 kJ/kg	46	6	48	0	0	0	100	
Other	hardwood (Birch)	13555 kJ/kg	46	6	48	0	0	0	100	
	Hardwood (Euca)	13555 kJ/kg		6	48	0	0	0	54	
	LIGNIN									
	softwood (Pine)	25300 kJ/kg	66	5,8	28,2	0	0	0	100	
	softwood (Spruce)	26900 kJ/kg	64	6	30	0	0	0	100	
	hardwood (Birch)	25110 kJ/kg	60	5,8	34,2	0	0	0	100	
	Hardwood (Euca)	25110 kJ/kg	60	5,8	34,2	0	0	0	100	
<b>J. Gullichsenin corresponding values are:</b>	softwoodlignin	26377 kJ/kg	64	6	30	0	0	0	100	
(Lignin heating value bit smaller)	hardwoodlignin	24702 kJ/kg	60	6	34	0	0	0	100	
org. acids heating value bit larger)	Acids from carbohydrates	17585 kJ/kg	46	6	48	0	0	0	100	
	RESINS									
	rosins and fatty acids	37710 kJ/kg	arvio=>	77	12	11	0	0	0	100
	OTHER ORGANIC COMPOUNDS									
	other organic compounds	18955 kJ/kg	arvio=>	45	4	51	0	0	0	100
	INORGANIC SUBSTANCES									
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	5790 kJ/kg	0	0	30	29	41	0	100	
	Na <sub>2</sub> S	12900 kJ/kg	0	0	0	59	41	0	100	
	Na <sub>2</sub> SO <sub>4</sub>	0 kJ/kg	0	0	45,1	32,4	22,5	0	100	
	NaOH	0 kJ/kg	0	2,5	40	57,5	0	0	100	
	Na <sub>2</sub> CO <sub>3</sub>	0 kJ/kg	11,3	0	45,3	43,4	0	0	100	
	Others	0 kJ/kg	0	0	0	0	0	100	100	
	SMELLY GASES AND VOLATILES									
	CH <sub>3</sub> SH	26100 kJ/kg				Pine	Spruce	Birch	Euca	Other
	CH <sub>3</sub> SCH <sub>3</sub>	30900 kJ/kg				39	41	40	45	0
	CH <sub>3</sub> SSCH <sub>3</sub>	23600 kJ/kg				30	30	37	25	0
	methanol	22300 kJ/kg				27	27	20	27	0
	turpentine	29200 kJ/kg				4	2	3	3	0
	REACTION HEATS	465 MJ/t pulp				softwood	softwood	hardwood	hardwood	0
						100	100	100	100	0

## Chemical compositions

		Pine	Spruce	Birch	Euca	Other
Cellulose	%	39	41	40	45	0
Hemicellulose	%	30	30	37	25	0
Lignin	%	27	27	20	27	0
Extractives	%	4	2	3	3	0
Summary		softwood	softwood	hardwood	hardwood	0
		100	100	100	100	0

### Softwood model for the Mill G

<b>Wood species in cooking</b>	1		<b>Composition of formed black liquor dry solids</b>				
Air dry unbleached cellulose	1427 t/24 h	355 days/y	Mill liquor	36,7 %	C	laboratory	
Yield in Oxygen delignification	96 %	H		3,8 %	H	38,23 %	Org acids 27,48 %
Yield from wood to dry unbleached cellulose	48 %	40-48 N		0,1 %		4,01 %	lignin 34,09 %
Pulp kappa before oxygen delignification	28	S		5,4 %	S	5,42 %	Soap 0,29 %
Pulp kappa after oxygen delignification	14	Na		17,5 %	Na	21,31 %	Other org 5,21 %
Washing efficiency unbleached pulp	99 %	K		1,5 %			Org. Na 8,17 %
Washing efficiency bleached pulp	99 %	Cl		0,3 %			NaOH 5,75 %
Soap recovery efficiency	80 %	O by diff		34,7 %	O	31,02 %	Na <sub>2</sub> S 11,89 %
Water created when wood acids are neutralized	100 kg/t Bleached pulp	Inorganics		24,7	SUM	68,98 %	Na <sub>2</sub> CO <sub>3</sub> 4,69 %
NCG generation during cook	3 % wood	S/(Na <sub>2</sub> +K <sub>2</sub> )		42,31			Na <sub>2</sub> SO <sub>4</sub> 2,44 %
Sulfur in NCG	2 kg/t Bleached pulp	Cl/(Na+K)		1,06			SUM 100,00 %
<b>White liquor</b>		K/(Na+K)		4,80			
Active alkali, Na <sub>2</sub> O-% per wood	18,6 %		<b>Chemical composition of wood</b>				
White liquor sulfidity	40 %		Cellulose	39 %			
White liquor dry solids	15 %		Hemicellulose	30 %			
Causticity	82 %		Lignin	27 %			
Reduction in white liquor	94 %		Extractives	4 %			
Black liquor dry solids	73 %		<b>Summary</b>	100			
<b>Oxidized White liquor</b>			Wood type	softwood			
Oxidized White liquor used in Oxygen delignification	200 kg/t Bleached pulp						
Methanol formation in Oxygen delignification	0,2 kg/t Bleached pulp						

### Heating value of black liquor dry-solids

Heat in to recovery boiler  
 Heat in to recovery boiler per second  
 Massflow to recovery boiler  
 Massflow to recovery boiler

### 15061 kJ/kg BLDS

23,849 GJ/t Bleached pulp  
 0,355 GJ/s  
 2153,5 tDS/24h  
 24,9 kgDS/s



<b>Organic compound:</b> Air dry bleached pulp pulp		1370,231 t/24h		2850
Dry bleached pulp pulp		1233 t/24h		2565
Dry unbleached cellulose		1285 t/24h		2700
Dry wood needed		2676 t/24h		5870
Wood needed to make 1000 kg unbleached		2083 kg/t Bleached pulp		2174
Loss as volatiles (including TRS-compounds)		63 kg/t Bleached pulp		65
TRS-compound loss (assumed as methylmerkaptan)		3 kg/t Bleached pulp		3
Water generated when acids in wood are neutralized		100 kg/t Bleached pulp		100
Organic compounds in Black liquor		1022 kg/t Bleached pulp		1110
Organic compounds in pulp		995 kg/t Bleached pulp		995
Lignin in wood to make 1 t of unbleached pulp	563 kg/t Bleached pulp	435		
Lignin in unbleached pulp	42 kg/t Bleached pulp	45		
Lignin in Black liquor	<b>520</b> kg/t Bleached pulp	390		
Tall oil from rosins and fatty acids	23 kg/t Bleached pulp	2		
Tall oil remains	0 kg/t Bleached pulp	0		
Tall oil recovered	18 kg/t Bleached pulp	2		
Tall oil in black liquor	<b>5</b> kg/t Bleached pulp	0		
Other organic compounds formation (4 % from wood)	83 kg/t Bleached pulp	87		
Other organic compounds to pulp	1 kg/t Bleached pulp	1		
Other organic compounds to Black liquor	<b>83</b> kg/t Bleached pulp	86		
Organic acids to Black liquor	<b>415</b> kg/t Bleached pulp	634		
<u>Sum of Organic compounds to Black liquor</u>	<u>1022</u> kg/t Bleached pulp	<u>1110</u>		
Lignin heating value	13167 kJ/kg Bleached pulp	9788	Heating vai kJ/BDt	14148
Rosins and fatty acids heating value	170 kJ/kg Bleached pulp	15	Heating vai kJ/BDt	174
Organic acids heating value	5746 kJ/kg Bleached pulp	8597	Heating vai kJ/BDt	7393
Other organic compounds heating value	1564 kJ/kg Bleached pulp	1632	Heating vai kJ/BDt	1254
<u>Sum of organic compounds heating value</u>	<u>20648</u> kJ/kg Bleached pulp	<u>20031</u>	Heating vai kJ/BDt	0
			<b>Heating v</b> kJ/BDt	<u>22968</u>
<b>White liquor</b> Active alkali, NaOH-% per dry wood		24 %		24
Active alkali kg/t unbleached pulp, Na <sub>2</sub> O		388 kg/t Bleached pulp		402
Active alkali kg/t unbleached pulp, NaOH		495 kg/t Bleached pulp		514
NaOH charge as Na <sub>2</sub> O		233 kg/t Bleached pulp		261
NaOH charge as NaOH		300 kg/t Bleached pulp		337
Na <sub>2</sub> S charge as Na <sub>2</sub> O		155 kg/t Bleached pulp		141
Na <sub>2</sub> S charge as NaOH		200 kg/t Bleached pulp		182

	Active alkali concentration, Na <sub>2</sub> O	116 g/l	112
	Active alkali concentration, NaOH	149 g/l	144
(estimate)	White liquor density	1169 g/l	1169
	Na <sub>2</sub> CO <sub>3</sub> in white liquor as Na <sub>2</sub> O	42 kg/t Bleached pulp	58
	Na <sub>2</sub> SO <sub>4</sub> in white liquor as Na <sub>2</sub> O	9 kg/t Bleached pulp	8
	<u>Sum of inorganic compounds in white liquor</u>	<u>588</u> kg/t Bleached pulp	<u>632</u>
	Sum of inorganic compounds in white liquor as Na <sub>2</sub> O	439 kg/t Bleached pulp	468
<b>Black liquor</b>	NaOH in black liquor	77 kg/t Bleached pulp	<u>114</u>
	Organically bound Na in black liquor	129 kg/t Bleached pulp	<u>129</u>
	Na <sub>2</sub> S in black liquor	188 kg/t Bleached pulp	<u>170</u>
	Na <sub>2</sub> CO <sub>3</sub> in black liquor	71 kg/t Bleached pulp	<u>97</u>
	Na <sub>2</sub> SO <sub>4</sub> in black liquor	21 kg/t Bleached pulp	<u>19</u>
	<u>Inorganic compounds in black liquor</u>	<u>487</u> kg/t Bleached pulp	<u>530</u>
	<b><u>Inorganic compounds, (Na<sub>2</sub>S heating value)</u></b>	<u>2428</u> kJ/kg Bleached pulp	<u>2199</u>
<b>Inorganic compounds in wood</b>	NaOH pulp	1 kg/t Bleached pulp	<u>1</u>
	Na in pulp organically bound	1 kg/t Bleached pulp	<u>1</u>
	Na <sub>2</sub> S pulp	2 kg/t Bleached pulp	<u>2</u>
	Na <sub>2</sub> CO <sub>3</sub> pulp	1 kg/t Bleached pulp	<u>1</u>
	Na <sub>2</sub> SO <sub>4</sub> pulp	0 kg/t Bleached pulp	0
	<u>Inorganic compounds pulp</u>	<u>5</u> kg/t Bleached pulp	5
Oxygen stage	<u>Black liquor dry solids from cooking</u>	<u>1509</u> kg/t Bleached pulp	1641
	<u>Bleached pulp formation</u>	<u>960</u> kg/t Bleached pulp	950
	<u>Bleached pulp inorganic compounds</u>	<u>5</u> kg/t Bleached pulp	6
	<u>Bleached pulp organic compounds</u>	<u>955</u> kg/t Bleached pulp	944
	<u>Loss of unbleached pulp during bleaching</u>	<u>40</u> kg/t Bleached pulp	50
	<u>Lignin in bleached pulp</u>	<u>23</u> kg/t Bleached pulp	31
	<u>Lignin dissolved to bleaching effluent</u>	<u>19</u> kg/t Bleached pulp	14

<b>oxidized White liquor</b>	<u>Metanol creation</u>	<u>0,2</u> kg/t Bleached pulp	0
	<u>Orgaanic acids to bleaching effluent</u>	<u>20</u> kg/t Bleached pulp	36
	<u>Organic compounds in bleaching effluent</u>	<u>40</u> kg/t Bleached pulp	50
	White liquor oxidizing reaction: $2\text{Na}_2\text{S} + 2\text{O}_2 + \text{H}_2\text{O} \Rightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaOH}$		
	Oxidized White liquor used in Oxygen delignification	200 kg/t Bleached pulp	200
	Unoxidized White liquor dry solids	15 %	15
	Unoxidized White liquor dry matter	150 kg/t WL unoxidated	150
	Unoxidized White liquor water	850 kg/t WL unoxidated	850
	Unoxidized White liquor Na <sub>2</sub> S-content	33 %	28
	Unoxidized White liquor NaOH-content	51 %	53
Unoxidized White liquor Na <sub>2</sub> CO <sub>3</sub> -content	12 %	16	
Unoxidized White liquor Na <sub>2</sub> SO <sub>4</sub> -content	4 %	3	
TOTAL	100 %	100	
White liquor oxidation reaction: $2\text{Na}_2\text{S} + 2\text{O}_2 + \text{H}_2\text{O} \Rightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaOH}$			

Na <sub>2</sub> S in one ton of unoxidized White liquor	50 kg/t WL unoxidated	42
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> in oxidation reaction	50 kg/t WL unoxidated	43
NaOH created in oxidation reaction	26 kg/t WL unoxidated	22
Water lost in oxidation reaction	6 kg/t WL unoxidated	5
NaOH in oxidized White liquor	102 kg/1021 kg WL oxidat	102
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> in oxidized White liquor	50 kg/1021 kg WL oxidat	43
Na <sub>2</sub> CO <sub>3</sub> in oxidized White liquor	18 kg/1021 kg WL oxidat	23
Na <sub>2</sub> SO <sub>4</sub> in oxidized White liquor	5 kg/1021 kg WL oxidat	5
Water in oxidized White liquor	844 kg/1021 kg WL oxidat	845
<i>Sum of oxidized White liquor</i>	1020 kg	1017
Oxygen delignification Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> oxidized fully to Na <sub>2</sub> SO <sub>4</sub> Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> + 2O <sub>2</sub> + 2NaOH => 2Na <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O		
Oxygen delignification NaOH used to oxidize thiosulfate	26 kg/1021 kg WL oxidat	21,55
Oxygen delignification Na <sub>2</sub> SO <sub>4</sub> created in oxidizing thiosulfate	91 kg/1021 kg WL oxidat	76,49
Oxygen delignification H <sub>2</sub> O created in oxidizing thiosulfate	6 kg/1021 kg WL oxidat	4,85
<i>Sum of water and inorganics in Bleaching residue</i>	1091 kg	1077

			Liquor analysis	Design value	Estimate from HHV
	NaOH in oxygen bleaching residue	14 kg/t Bleached pulp	15	Flow Tds/d	2260,2
	Na2S2O3 in oxygen bleaching residue	0 kg/t Bleached pulp	0	HHV MJ/kgds	15,06
	Na2CO3 in oxygen bleaching residue	3 kg/t Bleached pulp	4	C mass-%, c	36,65
	Na2SO4 in oxygen bleaching residue	18 kg/t Bleached pulp	15	H mass-%, c	3,81
	<u>Sum of Inorganic compounds to bleaching effluent</u>	35 kg/t Bleached pulp	34	N mass-%, c	0,10
				S mass-%, c	5,42
				Na mass-%, c	17,50
				K mass-%, c	1,50
				Cl mass-%, c	0,30
				Inorganics mass-%, c	24,7
	<b>Dry solids in Bleaching residue</b>	<b>75 kg/t Bleached pulp</b>	<b>84</b>	Dry solids %	73
<b>Bleaching residue heating value</b>	Lignin heating value in Bleaching residue	492 kJ/kg Bleached pulp	357	Air ratio -	1,164
	Organic acids heating value in Bleaching residue	282 kJ/kg Bleached pulp	482	NetHeat kW/kgds	9245
	Na2S2O3 heating value in in Bleaching residue	0 kJ/kg Bleached pulp	0	Air at 1.0 m3n/kgds	3,26
	<b>Bleaching residue heating value yhteensä</b>	<b>774 kJ/kg Bleached pulp</b>	<b>839</b>	Air at 1.x m3n/kgds	3,790
				Air/HHV m3n/MJ	0,216
				FG at 1.x m3n/kgds	4,690
				FG/HHV m3n/MJ	0,311
				FGdry at 1 m3n/kgds	4,058
	<b>Sum of Black liquor and Bleaching residue Dry solids</b>	<b>1584 kg/t Bleached pulp</b>	<b>1725</b>		
	<u><b>Black liquor total heating value</b></u>	<u><b>23849 kJ/kg Bleached pulp</b></u>	<u><b>23070</b></u>		
	<u><b>Black liquor Dry solids heating value</b></u>	<u><b>15061 kJ/kg BLDS</b></u>	<u><b>13375</b></u>		
	Dry solids to recovery boiler	1584 kg/t Bleached pulp	1725		
	Dry solids organic matter content	67,06 %	67		
	Black liquor to recovery boiler	2169 kg/t Bleached pulp	2464	Fg(wet) m3n/s	122,68
(estimate)	Black liquor density	1400 g/l	1400	kg/s	151,4
				Air m3n/s	85,2
				kg/s	109,2
	<b>Flue gases</b>	<b>6426 m3n(dry)/Adt</b>	<b>7712</b>	FG(dry) m3n/s	106,16
				kg/s	131,0
	<u><b>Heat to recovery boiler</b></u>	<u><b>23,85 GJ/t Bleached pulp</b></u>	<u><b>23,07</b></u>		
	"	<u><b>0,355 GJ/s</b></u>	<u><b>0,721</b></u>		
	<b>Moolmass</b>				
	Na2O	61,97894 g/mol			
	NaOH	39,99707 "			
	Alkali conversion NaOH	=	1,290666475 Na2O		

Wood species Compounds in liquor and their heating values

	SI heating value		C %	H %	O %	Na %	S %	Muut %	yht
Pine									
Spruce									
Birch									
Euca									
Other									
	ORG. ACIDS FROM CARBOHYDRATES								
	softwood (Pine)	13855 kJ/kg	46	6	48	0	0	0	100
	softwood (Spruce)	13340 kJ/kg	46	6	48	0	0	0	100
	hardwood (Birch)	13555 kJ/kg	46	6	48	0	0	0	100
	Hardwood (Euca)	13555 kJ/kg	46	6	48	0	0	0	100
	LIGNIN								
	softwood (Pine)	25300 kJ/kg	66	5,8	28,2	0	0	0	100
	softwood (Spruce)	26900 kJ/kg	64	6	30	0	0	0	100
	hardwood (Birch)	25110 kJ/kg	60	5,8	34,2	0	0	0	100
	Hardwood (Euca)	25110 kJ/kg	60	5,8	34,2	0	0	0	100
<b>J. Gullichsen:</b>	softwoodlignin	26377 kJ/kg	64	6	30	0	0	0	100
(Lignin heating value bit smaller	hardwoodlignin	24702 kJ/kg	60	6	34	0	0	0	100
org. acids heating value bit larger)	Acids from carbohydrates	17585 kJ/kg	46	6	48	0	0	0	100
	RESINS								
	rosins and fatty acids	37710 kJ/kg	arvio=>	77	12	11	0	0	100
	OTHER ORGANIC COMPOUNDS								
	other organic compounds	18955 kJ/kg	arvio=>	45	4	51	0	0	100
	INORGANIC SUBSTANCES								
	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	5790 kJ/kg	0	0	30	29	41	0	100
	Na <sub>2</sub> S	12900 kJ/kg	0	0	0	59	41	0	100
	Na <sub>2</sub> SO <sub>4</sub>	0 kJ/kg	0	0	45,1	32,4	22,5	0	100
	NaOH	0 kJ/kg	0	2,5	40	57,5	0	0	100
	Na <sub>2</sub> CO <sub>3</sub>	0 kJ/kg	11,3	0	45,3	43,4	0	0	100
	Others	0 kJ/kg	0	0	0	0	0	100	100

Chemical compositions

		Pine	Spruce	Birch	Euca	Other
CH <sub>3</sub> SH	26100 kJ/kg					
CH <sub>3</sub> SCH <sub>3</sub>	30900 kJ/kg	39	41	40	45	0
CH <sub>3</sub> SSCH <sub>3</sub>	23600 kJ/kg	30	30	37	25	0
methanol	22300 kJ/kg	27	27	20	27	0
turpentine	29200 kJ/kg	4	2	3	3	0
REACTION HEATS	465 MJ/t pulp					
		softwood	softwood	hardwood	hardwood	0
		100	100	100	100	
		Summary				

### Periodic measurement of emissions to air EU specific standards (Brinkmann et al. 2018, 127 – 130)

Parameter/ Substance(s) <sup>(1)</sup>	EN or ISO standard <sup>(1)</sup>	Monitoring methods	Measurement ranges and/or measurement limits <sup>(2)</sup>	Remarks
Ammonia (NH <sub>3</sub> )	No EN or ISO standard available	NA	NA	ISO standard being prepared (ISO/DIS 21877:2018); several national/industry standards are available, e.g. IS 11255- 6; NF X43-303; SCAQMD 207.1; UNICHIM 632; US EPA CTM-027; VDI 3878
Carbon monoxide (CO)	EN 15058:2017	Extraction, filtration and conditioning, followed by non-dispersive infrared spectrometry	Up to 400 mg/m <sup>3</sup> at large combustion plants (sampling duration of 30 min); Up to 740 mg/m <sup>3</sup> at waste (co-)incineration plants (sampling duration of 30 min)	—
Dinitrogen monoxide (N <sub>2</sub> O)	EN ISO 21258:2010	Extraction, filtration and conditioning, followed by non-dispersive infrared spectrometry	Up to 200 mg/m <sup>3</sup> <sup>(3)</sup>	—
Dust	EN 13284-1:2017	Extraction and filtration, followed by gravimetry	Up to 50 mg/m <sup>3</sup> , measurements typically at 5 mg/m <sup>3</sup> ; LoD: ~ 0.3 mg/m <sup>3</sup> (dry gases, sampling duration of 30 min), ~ 2 mg/m <sup>3</sup> (vapour-saturated gases, sampling duration of 30 min) <sup>(3)</sup>	—
Flow rate	EN ISO 16911-1:2013	<ul style="list-style-type: none"> <li>- Differential pressure (Pitot tube)</li> <li>- Vane anemometer</li> <li>- Tracer dilution</li> <li>- Tracer transit time</li> <li>- Calculation from energy consumption</li> </ul>	NS	CEN/TR 17078:2017 provides guidance on the application of EN ISO 16911-1:2013
Formaldehyde (CH <sub>2</sub> O)	No EN or ISO standard available	NA	NA	Several national/industry standards are available, e.g. CARB M 430; FD X43-319; NCASI CI/WP-98.01; US EPA M 0011 and M 316; VDI 3862-2 and -6

Parameter/ Substance(s) <sup>(1)</sup>	EN or ISO standard <sup>(1)</sup>	Monitoring methods	Measurement ranges and/or measurement limits <sup>(2)</sup>	Remarks
Gaseous chlorides	EN 1911:2010	Extraction and filtration, followed by absorption in water with subsequent chloride determination by a) silver potentiometric titration, b) mercury(II) thiocyanate spectrophotometry or c) ion chromatography	1 mg/m <sup>3</sup> to 5 000 mg/m <sup>3</sup> <sup>(3)</sup> ; LoD: ~ 0.2 mg/m <sup>3</sup> (sample gas volume of 0.4 m <sup>3</sup> to 0.5 m <sup>3</sup> , sampling duration of 2 h, method A); For water analysis: a): LoD: 0.5 mg/l to 1 mg/l b) and c): LoD: 0.05 mg/l to 0.1 mg/l	—
Gaseous fluorides	ISO 15713:2006	Extraction and filtration, followed by absorption in liquid phase with subsequent use of an ion-selective electrode	Up to 200 mg/m <sup>3</sup> ; LoD: ~ 0.1 mg/m <sup>3</sup> (sample gas volume of 0.1 m <sup>3</sup> )	—
Gaseous organic compounds	No EN or ISO standard available	NA	NA	CEN/TS 13649:2014 describes the determination of the mass concentration of individual gaseous organic compounds
Mercury (Hg)	EN 13211:2001	Extraction and filtration, followed by absorption in liquid phase (solution of KMnO <sub>4</sub> /H <sub>2</sub> SO <sub>4</sub> or K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> /HNO <sub>3</sub> ); subsequent digestion of the filter; final analysis of the aqueous samples by AAS	1 µg/m <sup>3</sup> to 500 µg/m <sup>3</sup> <sup>(3)</sup> ; LoD: 2.6 µg/m <sup>3</sup> (sample gas volume of 0.05 m <sup>3</sup> )	AC:2005 (Technical corrigendum)
Metals (As, Cd, Tl, Sb, Pb, Cr, Co, Cu, Mn, Ni, V)	EN 14385:2004	Extraction and filtration, followed by absorption in liquid phase (solution of H <sub>2</sub> O <sub>2</sub> /HNO <sub>3</sub> ); subsequent digestion of the filter; final analysis of the aqueous samples by AAS, ICP-OES or ICP-MS	5 µg/m <sup>3</sup> to 500 µg/m <sup>3</sup> (for each element) <sup>(3)</sup> ; Required LoD: ≤ 1 µg/m <sup>3</sup> for each element and sampling train; Resulting LoD: 5 µg/m <sup>3</sup> for the whole sampling train	—
Methane (CH <sub>4</sub> )	EN ISO 25139:2011	Extraction, filtration and conditioning, followed by gas chromatography with flame ionisation detection	Up to 1 500 mg/m <sup>3</sup>	—
Nitrogen oxides (NO <sub>x</sub> )	EN 14792:2017	Extraction, filtration and conditioning, followed by chemiluminescence (after conversion to NO and reaction with ozone)	Up to 1 300 mg/m <sup>3</sup> at large combustion plants; Up to 400 mg/m <sup>3</sup> at waste (co-)incineration plants	—
Odour	EN 13725:2003	Dynamic olfactometry	Measurements typically from 10 <sup>1</sup> ouE/m <sup>3</sup> to 10 <sup>7</sup> ouE/m <sup>3</sup> (including predilution); Detection threshold: 1 ouE/m <sup>3</sup>	AC:2006 (Technical corrigendum)
Oxygen (O <sub>2</sub> )	EN 14789:2017	Extraction, filtration and conditioning, followed by paramagnetism	3 vol-% to 21 vol-% (sampling duration of 30 min) <sup>(3)</sup> <sup>(4)</sup> <sup>(5)</sup>	—
PM <sub>10</sub> /PM <sub>2.5</sub>	EN ISO 23210:2009	Impactors, followed by gravimetry	LoD: PM <sub>10</sub> : 0.4 mg/m <sup>3</sup> (sample gas volume: 1 m <sup>3</sup> , sampling duration of ~ 30 min) LoD: PM <sub>2.5</sub> : 0.3 mg/m <sup>3</sup> (sample gas volume: 1 m <sup>3</sup> , sampling duration of ~ 30 min)	—



Parameter/ Substance(s) <sup>(1)</sup>	EN or ISO standard <sup>(1)</sup>	Monitoring methods	Measurement ranges and/or measurement limits <sup>(2)</sup>	Remarks
Dioxin-like PCBs	EN 1948-4:2010	Sampling according to EN 1948-1, followed by extraction and clean-up according to EN 1948-2 and subsequent identification and quantification using isotope dilution gas chromatography with mass spectrometry	LoD: 0.11 pg WHO-TEQ/m <sup>3</sup> to 0.57 pg WHO-TEQ/m <sup>3</sup> , LoQ: 0.20 pg WHO-TEQ/m <sup>3</sup> to 1.37 pg WHO-TEQ/m <sup>3</sup> (depending on sampling method) <sup>(3)</sup>	A1:2013 (Amendment 1)
PCDDs/PCDFs	EN 1948-1:2006 EN 1948-2:2006 EN 1948-3:2006	EN 1948-1: Sampling by filter/condenser method, dilution method or cooled probe method EN 1948-2: Extraction and clean-up EN 1948-3: Identification and quantification using isotope dilution gas chromatography with mass spectrometry	Measurements typically at 0.1 ng I-TEQ/m <sup>3</sup> ; LoQ: 0.1 pg/m <sup>3</sup> to 8.8 pg/m <sup>3</sup> for individual congeners <sup>(3)</sup> (corresponds to a LoQ of 1.2 pg I-TEQ/m <sup>3</sup> to 3.7 pg I-TEQ/m <sup>3</sup> )	CEN/TS 1948-5:2015 describes the long-term sampling of PCDDs/PCDFs and PCBs
Polycyclic aromatic hydrocarbons (PAHs)	ISO 11338-1:2003 ISO 11338-2:2003	ISO 11338-1: Sampling by the dilution method, the heated filter/condenser/adsorber method or the cooled probe/adsorber method ISO 11338-2: Sample preparation, clean-up and determination by high-performance liquid chromatography (HPLC) or gas chromatography mass spectrometry (GC-MS)	LoD (16 US EPA PAH): 0.1 µg/m <sup>3</sup> to 1 µg/m <sup>3</sup> for 6 m <sup>3</sup> sample volume and a dilution factor of 100	—
Sulphur oxides (SO <sub>x</sub> )	EN 14791:2017	Extraction and filtration, followed by absorption in aqueous H <sub>2</sub> O <sub>2</sub> solution with subsequent sulphate determination via a) ion chromatography or b) titration	a) Ion chromatography: 0.5 mg/m <sup>3</sup> to 2 000 mg/m <sup>3</sup> (sampling duration of 30 min) <sup>(3)</sup> <sup>(4)</sup> ; LoQ: ≥ 0.1 mg/m <sup>3</sup> (flow rate of 1 l/min, 100 ml of absorption solution, sampling duration of 30 min) b) Titration: 5 mg/m <sup>3</sup> to 2 000 mg/m <sup>3</sup> (sampling duration of 30 min) <sup>(3)</sup> <sup>(4)</sup> ; LoQ ≥ 2.2 mg/m <sup>3</sup> (flow rate of 1 l/min, 100 ml of absorption solution, sampling duration of 30 min)	—
Temperature	No EN or ISO standard available	NA	NA	—
Total volatile organic carbon (TVOC)	EN 12619:2013	Extraction and filtration, followed by flame ionisation detection	Up to 1 000 mg/m <sup>3</sup>	—
	EN ISO 13199:2012	Extraction and filtration, followed by catalytic conversion and NDIR	From about 70 mg/m <sup>3</sup> to 600 mg/m <sup>3</sup>	Not applicable to combustion processes

Parameter/ Substance(s) <sup>(1)</sup>	EN or ISO standard <sup>(1)</sup>	Monitoring methods	Measurement ranges and/or measurement limits <sup>(2)</sup>	Remarks
Water vapour	EN 14790:2017	- Extraction and filtration, followed by adsorption or condensation/adsorption with subsequent gravimetry - Temperature method for vapour-saturated gases	4 vol-% to 40 vol-%	—
<p><sup>(1)</sup> Non-exhaustive list.  <sup>(2)</sup> Under standard conditions, i.e. dry gas, 273.15 K, 101.3 kPa, at the reference O<sub>2</sub> concentration.  <sup>(3)</sup> Validated during field trials in waste (co-)incineration plants.  <sup>(4)</sup> Validated during field trials in large combustion plants.  <sup>(5)</sup> Validated on a recognised test bench.</p> <p>NB: AAS = atomic absorption spectrometry; GC-MS = gas chromatography mass spectrometry; HPLC = high-performance liquid chromatography; ICP-OES = inductively coupled plasma optical emission spectrometry; ICP-MS = inductively coupled plasma mass spectrometry; I-TEQ = international toxic equivalent; LoD = limit of detection; LoQ = limit of quantification; NA = not applicable; NDIR = non-dispersive infrared spectrometry; NS = not specified.</p>				

\*Not all the standards or emissions mentioned here are needed or measured actually in Finnish RBs.

## Automatic measurement system specific standards (Brinkmann et al. 2018, 131 – 132)

Parameter/ Substance(s)	Monitoring methods	Certified measurement ranges and measurement limits <sup>(1)</sup> <sup>(2)</sup> <sup>(3)</sup>	Certification and calibration standards	EN or ISO standard for SRM
Ammonia (NH <sub>3</sub> )	FTIR, NDIR with GFC, TDL	Lowest range: ≤ 0.4 mg/m <sup>3</sup> (LoQ req.) to 5 mg/m <sup>3</sup> <sup>(2)</sup> Highest range: up to 500 mg/m <sup>3</sup>	Generic standards <sup>(4)</sup>	No EN or ISO standard available
Carbon monoxide (CO)	FTIR, NDIR	Lowest range: ≤ 4 mg/m <sup>3</sup> (LoQ req.) to 50 mg/m <sup>3</sup> Highest range: up to 10 g/m <sup>3</sup>	Generic standards <sup>(4)</sup>	EN 15058:2017
Dinitrogen monoxide (N <sub>2</sub> O)	FTIR, NDIR	Lowest range: ≤ 1.6 mg/m <sup>3</sup> (LoQ req.) to 20 mg/m <sup>3</sup> Highest range: up to 9.8 g/m <sup>3</sup> (given as 5 000 ppm)	Generic standards <sup>(4)</sup>	EN ISO 21258:2010
Dust	Light attenuation or scattering, triboelectric	Lowest range: ≤ 0.12 mg/m <sup>3</sup> (LoQ req.) to 1.5 mg/m <sup>3</sup> (given as 5 scattered light units) <sup>(5)</sup> Highest range: up to 300 mg/m <sup>3</sup> (given as 20 000 scattered light units)	Generic standards <sup>(4)</sup> and EN 13284-2:2017	EN 13284-1:2017
Flow rate	Ultrasound, differential pressure (Pitot tube), IR cross-correlation of turbulence, thermal mass flow	Lowest range: 1.6 m/s (LoQ req.) to 20 m/s Highest range: up to 60 m/s	Generic standards <sup>(4)</sup> and EN ISO 16911-2:2013	EN ISO 16911-1:2013
Hydrogen chloride (HCl)	FTIR, NDIR with GFC, TDL	Lowest range: ≤ 0.8 mg/m <sup>3</sup> (LoQ req.) to 10 mg/m <sup>3</sup> <sup>(2)</sup> Highest range: up to 5.0 g/m <sup>3</sup>	Generic standards <sup>(4)</sup>	EN 1911:2010
Hydrogen fluoride (HF)	FTIR, TDL	Lowest range: ≤ 0.08 mg/m <sup>3</sup> (LoQ req.) to 1 mg/m <sup>3</sup> <sup>(2)</sup> Highest range: up to 300 mg/m <sup>3</sup>	Generic standards <sup>(4)</sup>	ISO 15713:2006
Methane (CH <sub>4</sub> )	FID, FTIR, NDIR	Lowest range: ≤ 0.6 mg/m <sup>3</sup> (LoQ req.) to 7.5 mg/m <sup>3</sup> <sup>(2)</sup> Highest range: up to 500 mg/m <sup>3</sup>	Generic standards <sup>(4)</sup> and EN ISO 25140:2010	EN ISO 25139:2011
Mercury (Hg)	AAS, DOAS	Lowest range: ≤ 0.4 µg/m <sup>3</sup> (LoQ req.) to 5 µg/m <sup>3</sup> <sup>(2)</sup> Highest range: up to 1 mg/m <sup>3</sup>	Generic standards <sup>(4)</sup> and EN 14884:2005	EN 13211:2001
Nitrogen oxides (NO <sub>x</sub> ) <sup>(6)</sup>	Chemiluminescence, FTIR, NDIR, NDUV, DOAS	Lowest range: ≤ 1.6 mg/m <sup>3</sup> (LoQ req.) to 20 mg/m <sup>3</sup> <sup>(2)</sup> Highest range: up to 7.5 g/m <sup>3</sup>	Generic standards <sup>(4)</sup>	EN 14792:2017
Oxygen (O <sub>2</sub> )	Paramagnetism, electrochemical cell, zirconia (ZrO <sub>2</sub> )	Lowest range: ≤ 0.8 vol-% (LoQ req.) to 5 vol-% Highest range: up to 25 vol-%	Generic standards <sup>(4)</sup>	EN 14789:2017

Parameter/ Substance(s)	Monitoring methods	Certified measurement ranges and measurement limits <sup>(1)</sup> <sup>(2)</sup> <sup>(3)</sup>	Certification and calibration standards	EN or ISO standard for SRM
Sulphur dioxide (SO <sub>2</sub> )	FTIR, NDIR, NDUV, DOAS	Lowest range: ≤ 0.8 mg/m <sup>3</sup> (LoQ req.) to 10 mg/m <sup>3</sup> <sup>(3)</sup> Highest range: up to 8.0 g/m <sup>3</sup>	Generic standards <sup>(4)</sup>	EN 14791:2017
Temperature	Thermocouples, pyrometry	400 °C to 1 300 °C (one certified AMS)	Generic standards <sup>(4)</sup>	No specific EN or ISO standard for measurements in air available
Total volatile organic carbon (TVOC)	FID	Lowest range: ≤ 1.2 mg/m <sup>3</sup> (LoQ req.) to 15 mg/m <sup>3</sup> Highest range: up to 2.0 g/m <sup>3</sup>	Generic standards <sup>(4)</sup>	EN 12619:2013
Water vapour	FTIR, NDIR with GFC, TDL	Lowest range: ≤ 2 vol-% (LoQ req.) to 25 vol-% <sup>(5)</sup> Highest range: up to 50 vol-%	Generic standards <sup>(4)</sup>	EN 14790:2017

<sup>(1)</sup> The certification process is described in Section 4.3.2.2.1.  
<sup>(2)</sup> Under standard conditions, i.e. dry gas, 273.15 K, 101.3 kPa, at the reference O<sub>2</sub> concentration.  
<sup>(3)</sup> LoQs are specified as performance criteria and are derived from four times the performance criterion for the repeatability standard deviation (RSD) at zero in laboratory tests according to EN 15267-3:2007. For the flow rate, particulate matter, and gaseous compounds except oxygen, the performance criterion for the RSD is ≤ 2.0 % of the upper limit of the certification range. For oxygen, the performance criterion for the RSD is ≤ 0.20 vol-%. For the flow rate, the RSD applies at the lower reference point (instead of applying at zero). Actual LoQs may be (much) lower than the required performance.  
<sup>(4)</sup> EN15267-1:2009, EN15267-2:2009, EN15267-3:2007 and EN 14181:2014.  
<sup>(5)</sup> At the beginning of 2018, this measurement range was certified for one AMS. The other AMS were certified for higher ranges.  
<sup>(6)</sup> AMS for measuring NO and NO<sub>2</sub> separately are also available.  
NB: AAS = atomic absorption spectrometry; DOAS = differential optical absorption spectroscopy; FID = flame ionisation detection; FTIR = Fourier transform infrared spectrometry; GFC = gas filter correlation; LoQ = limit of quantification; NDIR = non-dispersive infrared spectrometry; NDUV = non-dispersive UV spectrometry; req. = requirement; SRM = standard reference method; TDL = tunable diode laser absorption spectrometry.

\*Not all the standards or emissions mentioned here are needed or measured actually in Finnish RBs.