LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
LUT School of Energy Systems
Sustainability science and solutions

Verifying the pulp mill atmospheric emissions from the recovery boiler

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ABSTRACT

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Master's thesis

Verifying the pulp mills atmospheric emissions from the recovery boiler

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Examiner: Professor Risto Soukka
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Finnish pulp and paper industry has a long history and its effect on the Finnish economic life is significant. Similar to every other industry, also Finnish pulp mills produce emissions to air. This Master's thesis examines the differences on reported results to calculated emissions in the real pulp mills. The focus of the study is the difference caused by measurements in recovery stack gas flows. The reported results were verified against created model of combustion and the differences between reported and computed are highlighted. Those pulps and their emission balances would be represented and this research is aimed to implement actions in emission reporting in the mills operations. Methods in emission measurement technology are presented. Measurement of emissions is part of environmental protection at the factories which is regulated by the BREF and other documents. Usually measurement happens just before end of the pipe after regulatory air pollution control engineering devices in various locations from the stack and its gas flow. Flue gas amount will be reported in same oxygen reference level and averaging, putting the actual flue gas amount in later report. Forest industry in Finland uses approximately 150 million euros to environmental protection every year.

YHTEENVETO

Lappeenrannan Teknillinen Yliopisto
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Sellutehtaiden soodakattiloiden ilmapäästöjen tarkistus

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Suomalaisella sellu – ja paperiteollisuudella on pitkä historia ja sen vaikutus suomalaiseen talouselämään on suuri. Kuten jokainen teollisuuden ala, myös Suomen massatehtaat aiheuttavat ilmapäästöjä. Tässä diplomityössä tutkitaan syitä raportoitujen päästöjen eroihin aidoissa olemassa olevissa tehtaissa. Tutkimus keskittyy savukaasuvirtauksen määrittämiseen. Vertaillaan tehtaan päästömittauksien perusteella raportoimia tuloksia ja tehtyjen tehtaan massataseen laskennan avulla saatuja arvoja. Esittämällä sellutehtaiden soodakattiloiden päästötaseet voidaan vaikuttamaan tehtaiden toimintaan ja päästöjen raportointiin tulevaisuudessa. Esitetään päästömittauksen perusperiaatteet. Päästömittaus on osana tehtaiden ympäristönsuojelua ja sitä ohjataan muun muassa BREF asiakirjalla. Yleensä päästömittaus tapahtuu juuri ennen piipun päätä savukaasupesurien ja -suodattimien jälkeen sen sisällä virtaavasta savukaasusta. Savukaasunmäärä tulee raportoida samassa määrätyssä happipitoisuudessa ja keskiarvoistus sekä määrän ilmoittaminen tulee tehdä oikein tulevissa raportoinneissa. Metsäteollisuus käyttää vuodessa noin 150 miljoona euroa luonnonsuojelutyöhön.

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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
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

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_x and sulphur emissions (Knowpulp 2018, Dahl 2008, 16). Flue gases contain mainly combustion products and air (N_2, CO_2, H_2O, O_2), 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_2SO_4. 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 to 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.

This Master's thesis looks at statistics and models kraft boilers flue gas amounts in respect to wood species in Finland. These wood species are mainly birch and pine. Off-gas amount represent amount of combusted mass to gases that exit stack flue. Verifying the amount of combustion gas flow is important as verifying of concentration of pollutant depends from it, but seemingly work still needs be done to certify that flue-gas flow-rate in respect to produced pulp, which was reported in 2008 from most of the pulp mills in EU. 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 for mathematical modelling which involves flow calculation). Statistics offer also year 2016 mill specific air pollutant emissions and pulp production rates.

There has been more and more attention towards RBs flue gas emissions and monitoring during the last 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. 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.

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 have been reduced significantly during the past years. In 15 year period 70 – 80 % is been reduced (Knowpulp 2010). Figure 1 presents current paper mills, paperboard mills and pulp mills in Finland in year 2017.

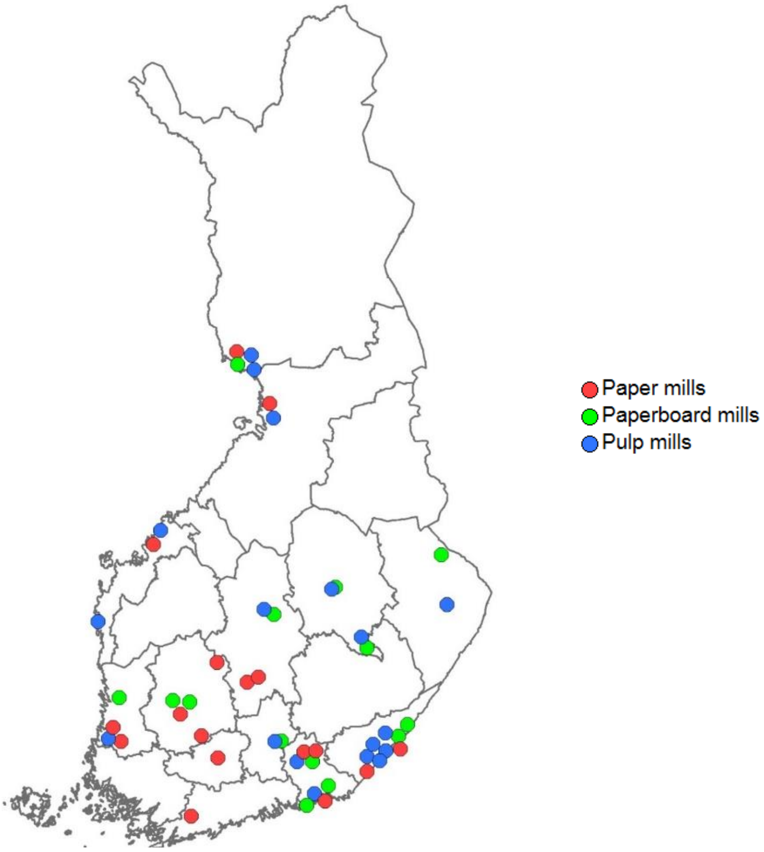


Figure 1 Finnish paper-, paperboard- and chemical pulp mills that are in operation in 2017 (Finnish Forest Industries 2017).

CO_2 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_2-emissions due to LULUCF should be carefully observed and monitored.

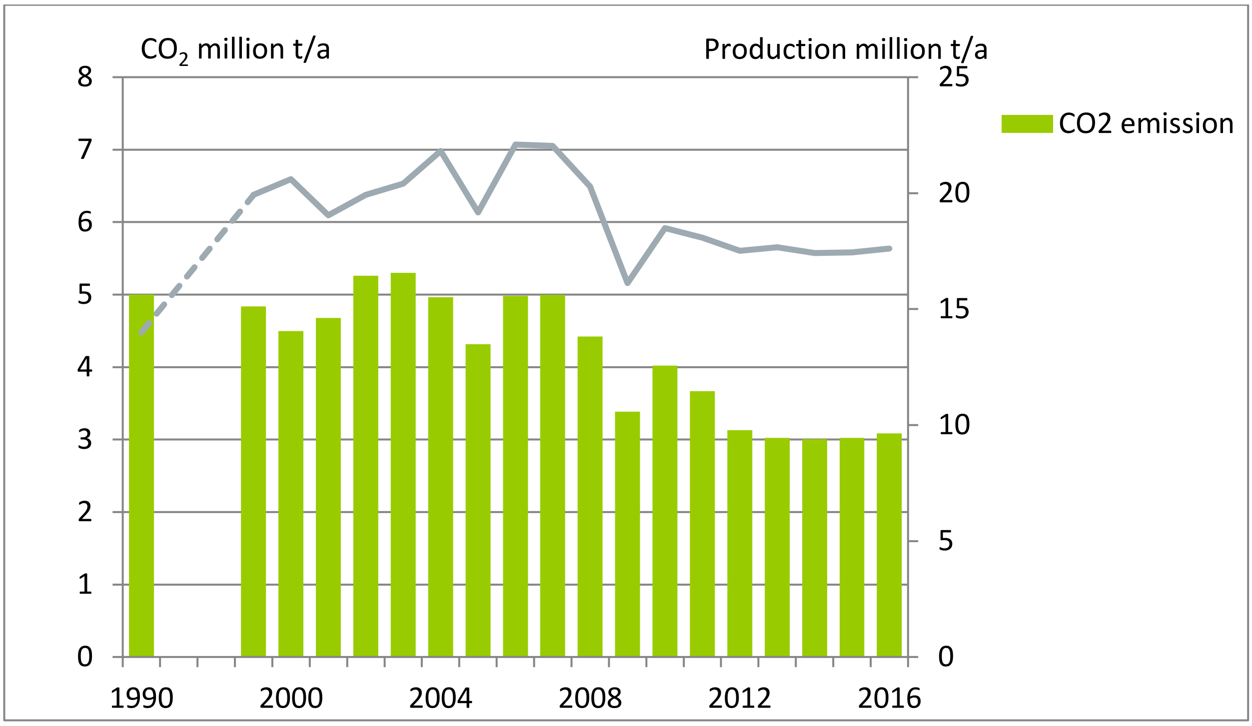


Figure 2 Fossil CO_2 emissions from the pulp and paper industry in Finland (Finnish Forest Industries 2017)

Latest estimate from year 2016 in Figure 2 shows 9,8 million tons of CO_2 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).

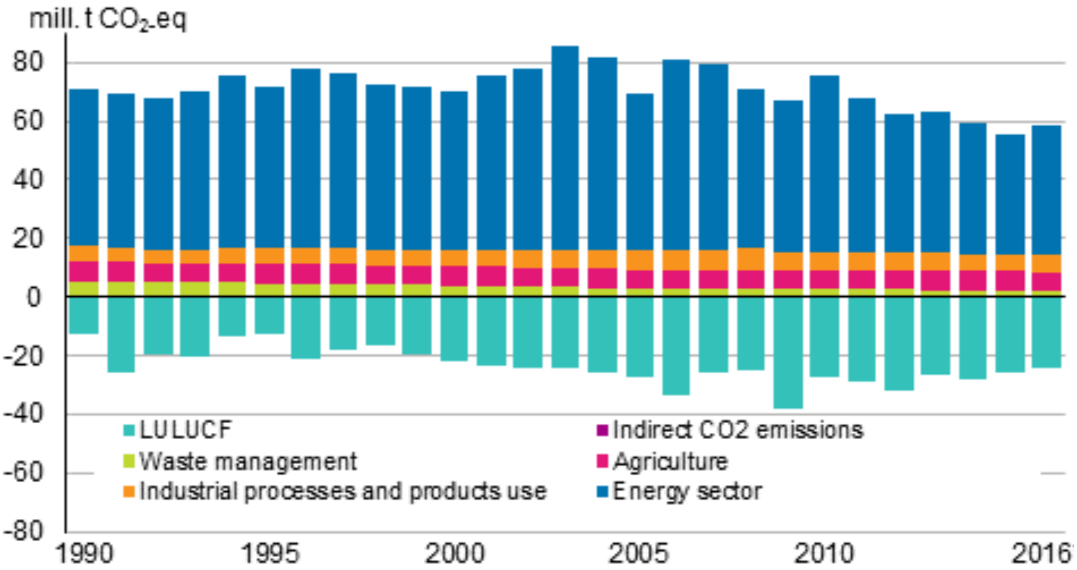


Figure 3 Sectors and their amount of GHG emissions in Finland from year 1990 to 2016 (Statistics Finland 2017)

Environmental awareness in Finnish pulp mills and energy efficiency has resulted in increasing the values of companies – better operation results more pulp to the market. This implies sale and expenditures per produced ton of pulp or bio-based materials becomes lower. Over the years, focusing on environmental technology improvements have contribute great savings to the mills environment. 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 separated lignin.

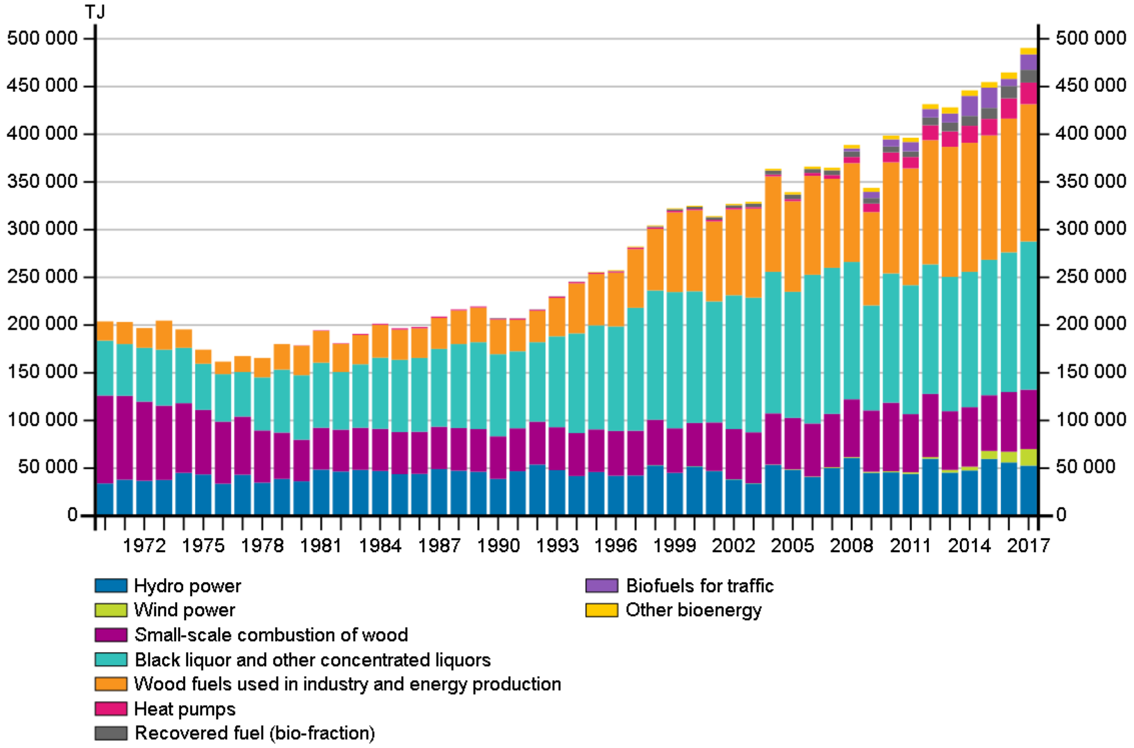


Figure 4 Consumption of renewable energy sources in Finland (Findicator 2017.)

In Finland year 2008 there were 15 kraft recovery boilers with startup time from 1965 to 2008 and 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. Other significant type of biomass boiler is the bark combustion boiler. (Statistics Finland 2017)

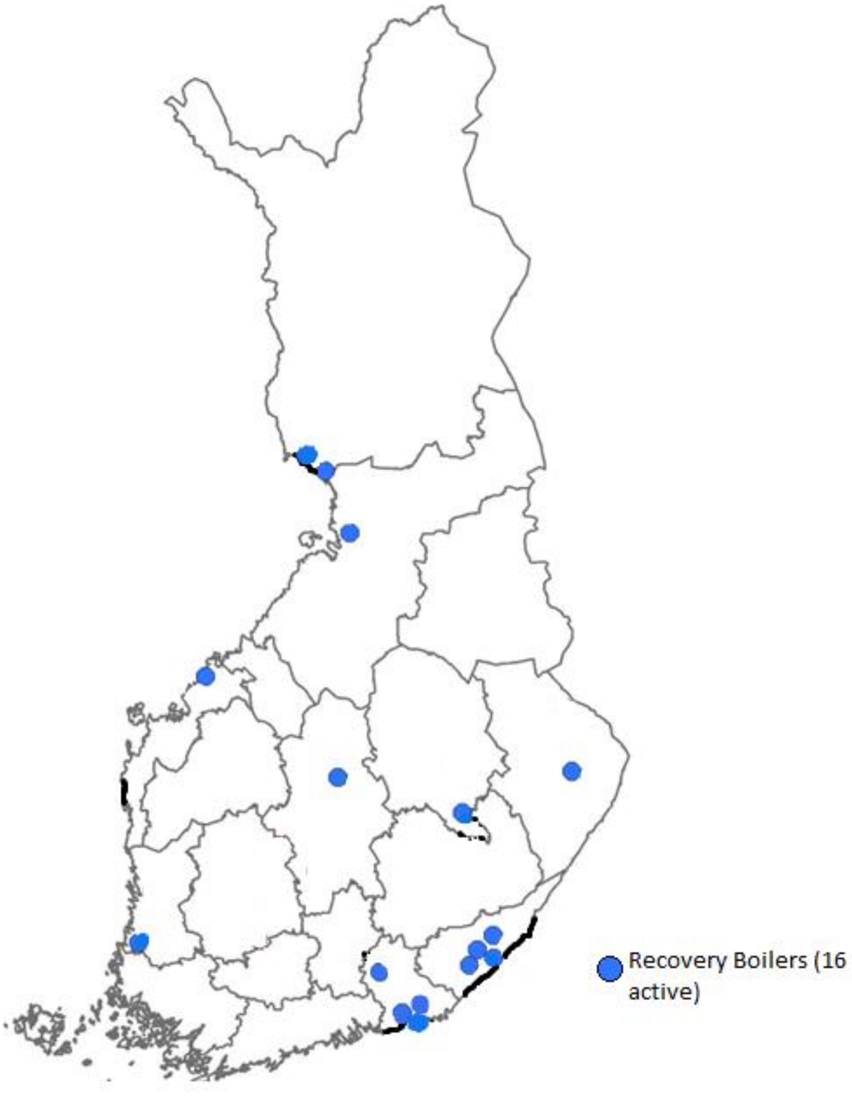


Figure 5 RBs active in Finland 2018 – there are 16 of them operating. Sunila mill and Imatra mills have two operating boilers in operation.

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. Statistically are usually written spruce, pine and softwoods.

Wood is a three-dimensional biopolymer composite composed of an interconnected networks of cellulose, hemicellulose and lignin and minor amounts of extractives and inorganics. Naturally, 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 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	*Pinus Sylvestris*
spruce, norway spruce	*Picea abies*
birch, silver birch, downy birch	*Betula pubescens* and *Betula verrucosa*
aspen	*Populus tremula, Populos tremuloides* *and Populus tremula × tremuloides Michx*
alder, grey alder, black alder	*Almus incana, Almus glutinosa*

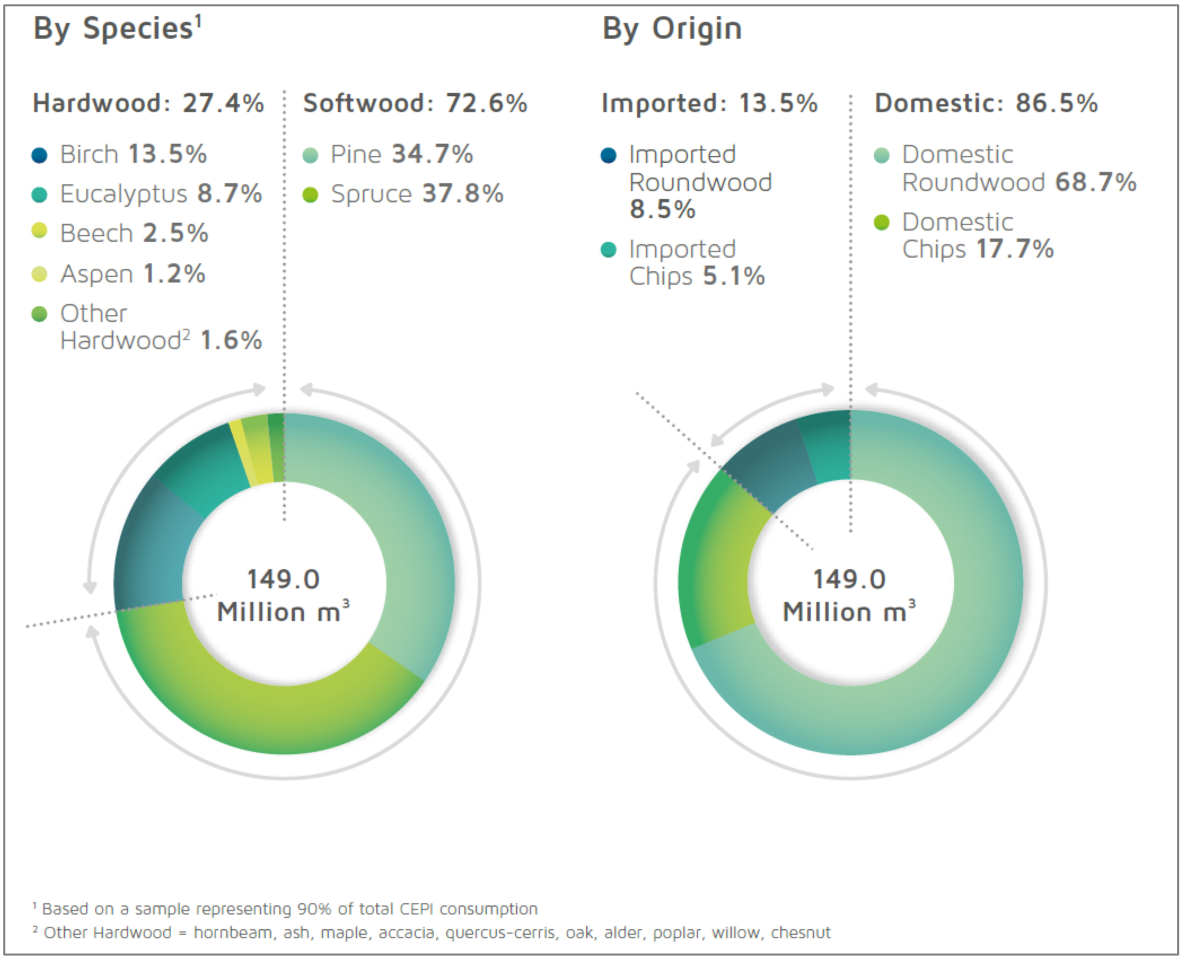
From the table 1 presented species pine, spruce and birch are the main three by total mass. In table 2 is presented the main trees chemical composition.

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

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



[1] Based on a sample representing 90% of total CEPI consumption

[2] Other Hardwood = hornbeam, ash, maple, accacia, quercus-cerris, oak, alder, poplar, willow, chesnut

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 matter of the 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.

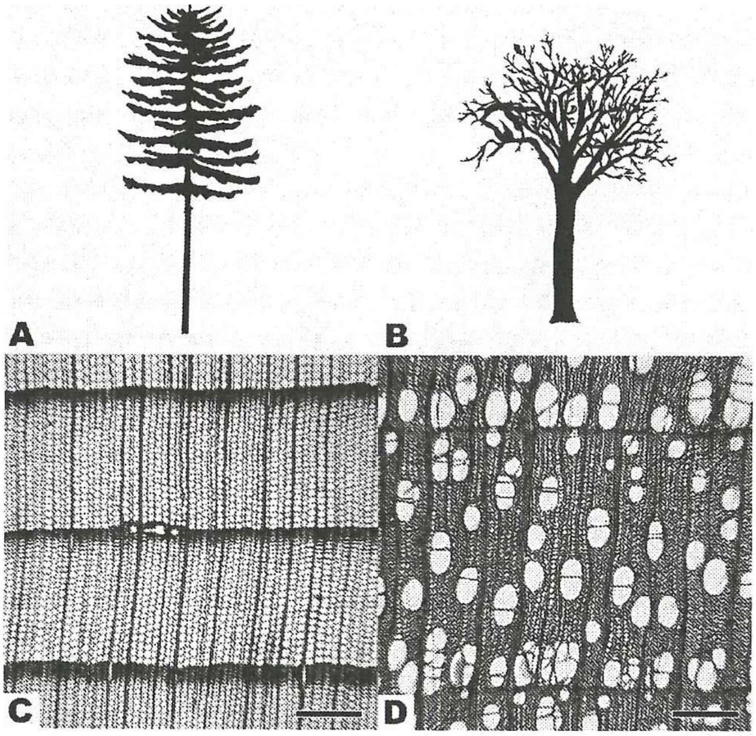


Figure 7 A softwood configuration B hardwood configuration C Douglas firs transverse section, typical softwood D transverse section of yellow birch a typical hardwood. Scale bar in C and D is 300 µm. (Wiedenhoeft 2005, 11)

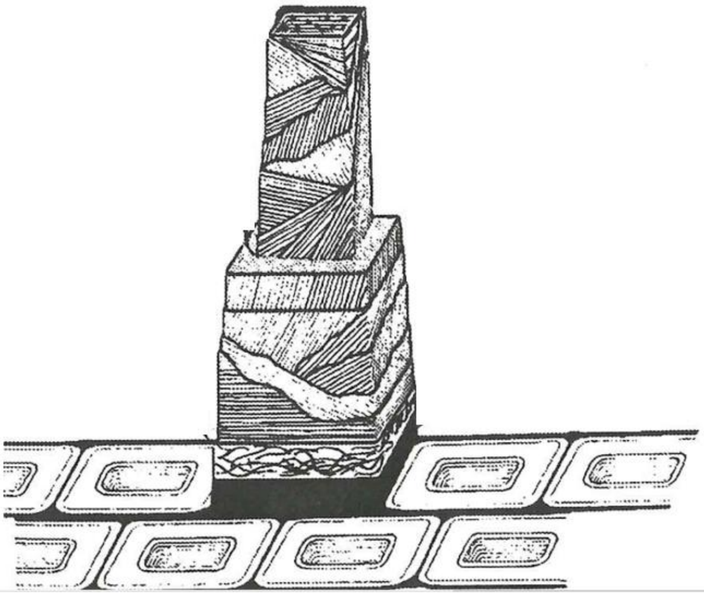


Figure 8 Schematic picture of cell wall of the scots pine (Rowell et al. 2005, 51)

Softwoods has resin canals. around those canals are epithelial cells (Jääskeläinen&Sundqvist 2007, 41). Jupiner tree has not resin canals, but pine and spruce have resin canals, though all softwood 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 to grow certain way and interact with the environment, drawing to its parts different chemicals more than other to 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 effectively water radially in hardwoods. (Jääskeläinen&Sundqvist 2007, 41–46)

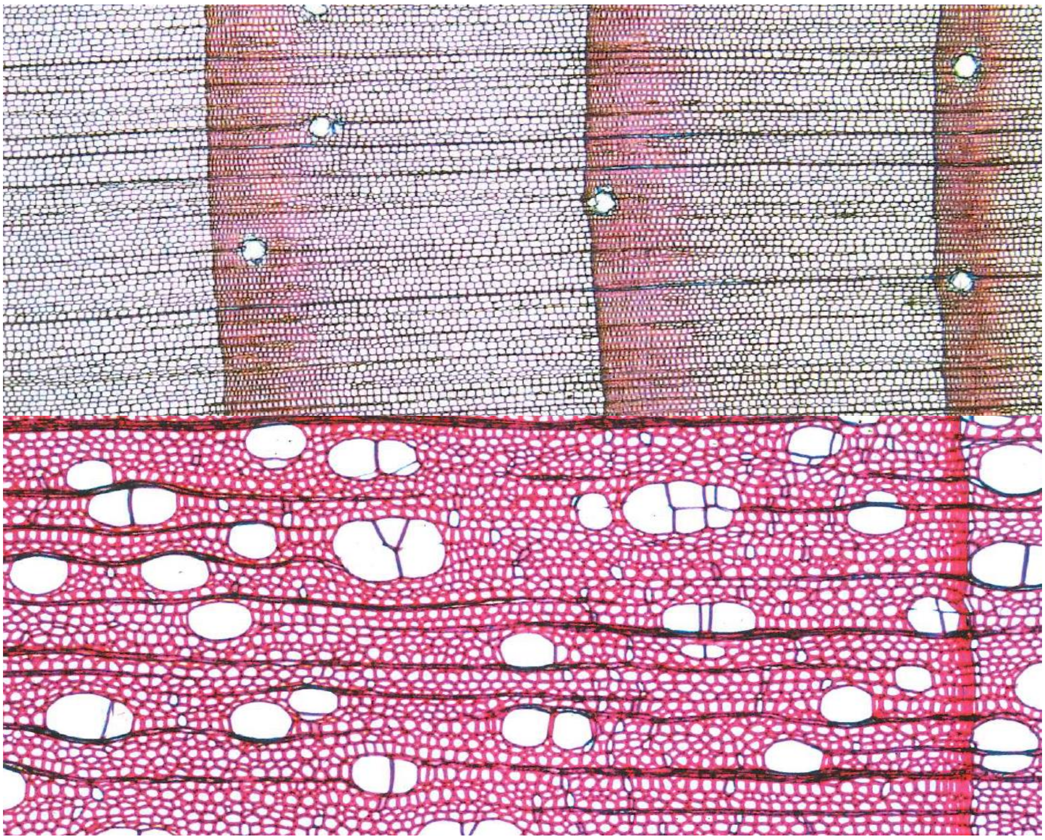


Figure 9 Upper crosscut is pine, down crosscut is birch. Birch has main part is fibre. Pine has those resin canals white holes, difference is macroscopic between these two species (Kärkkäinen 2007, 39, 49). Photos by Pekka Saranpää.

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 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.

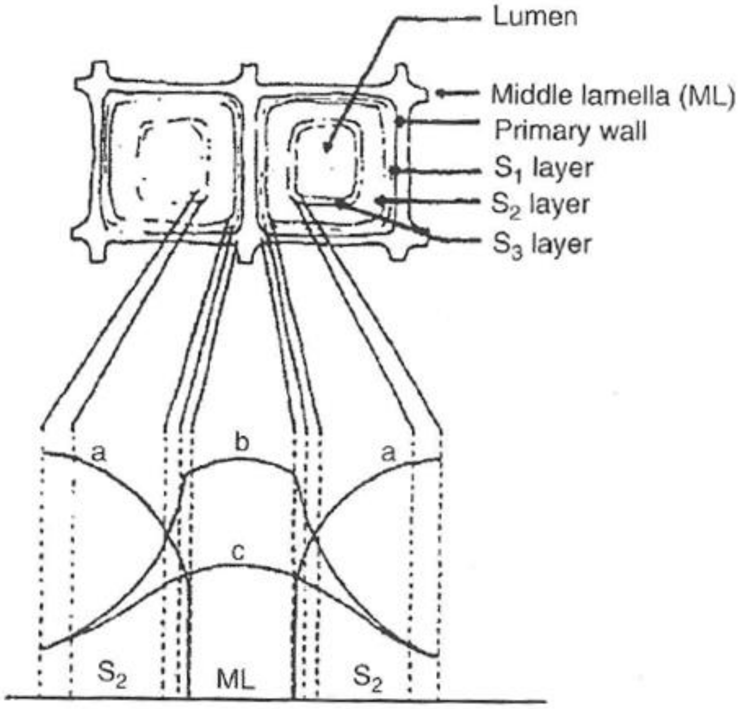


Figure 10 Wood cell has relative amounts of a) cellulose b) lignin c) hemicellulose Lumen, Middle lamella primary wall, S_1 layer S_2 layer and S_3 layer are typical in literature presented wood cell division. (Williams. 2005, 148)

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.

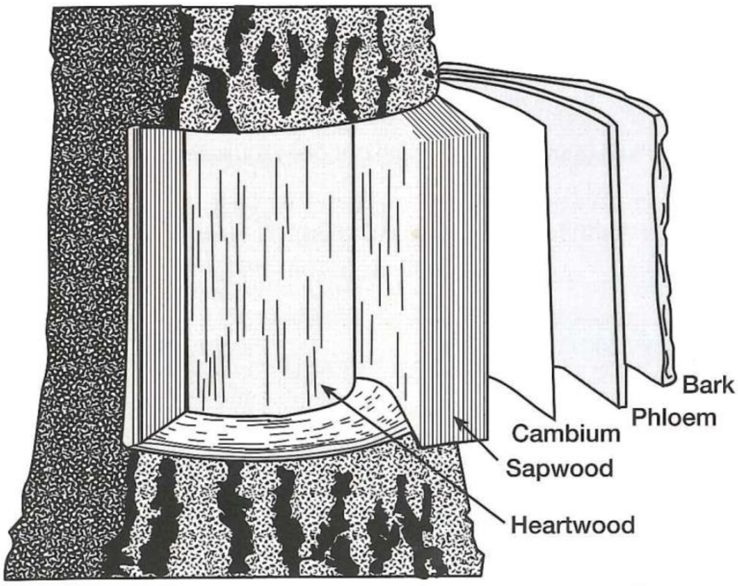


Figure 11 Bark is debarked before pulping. **(**Kellomäki 2009, 21)

Direction from 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 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. Usually this kind of logs are 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 diagram made from the table 3. Almost half of the whole raw material was softwood origin.

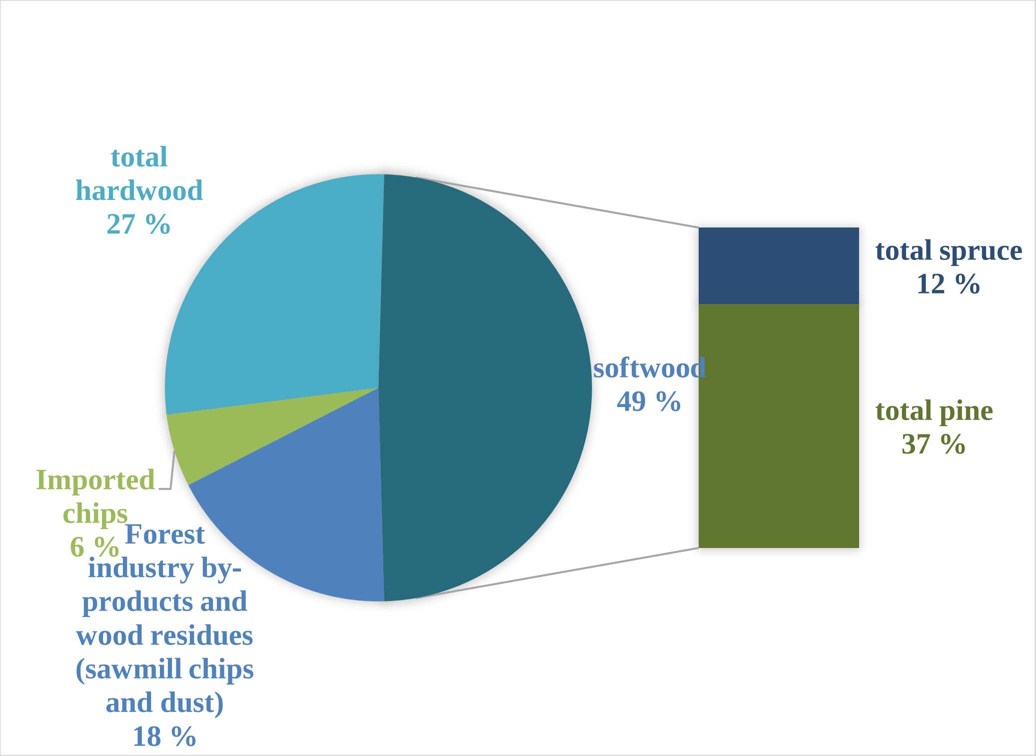
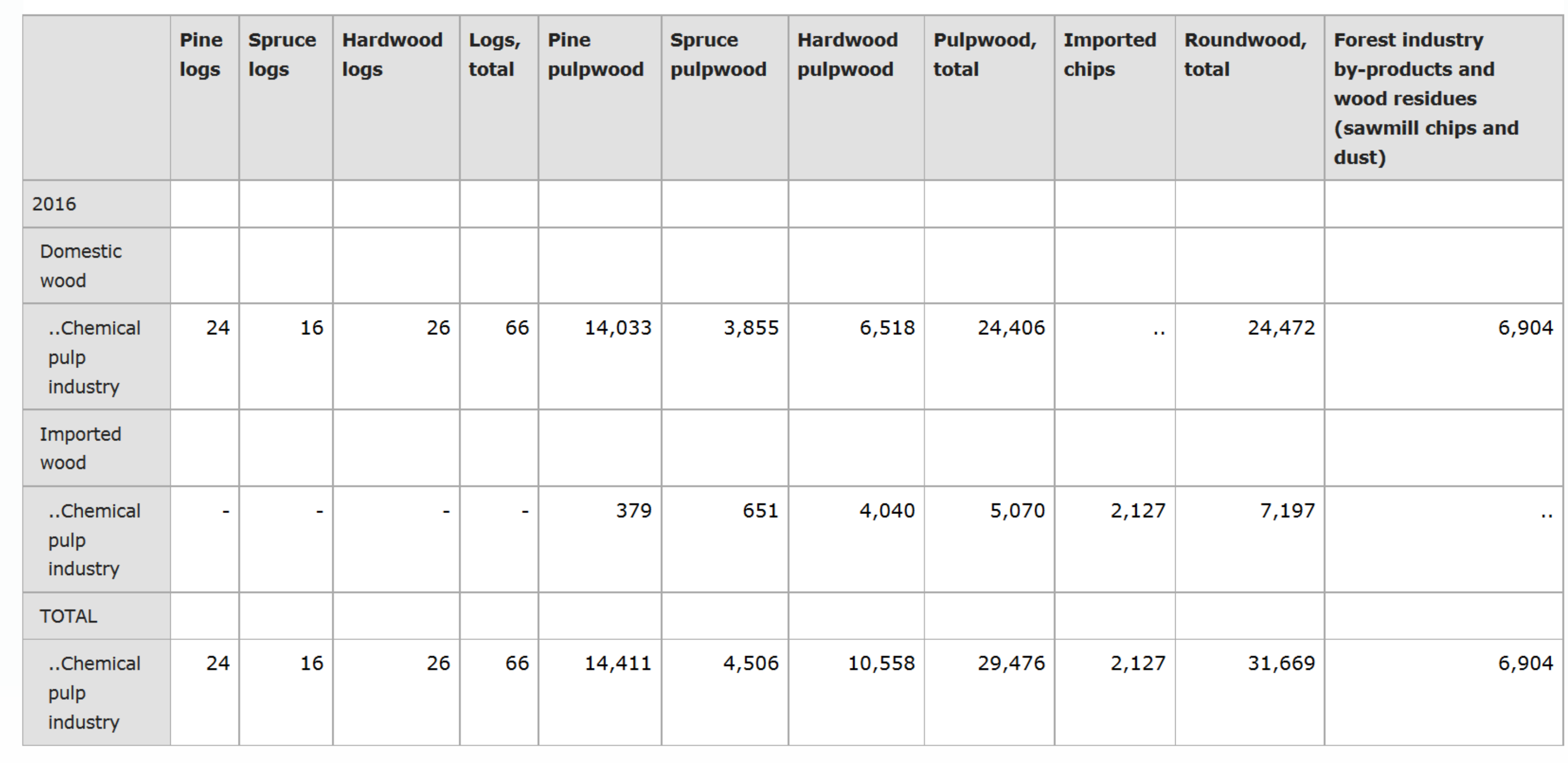


Figure 12 Wood raw materials in chemical pulps in Finland year 2016 (Luke, 2017)

Table 3 Forest industries´ wood consumption (1000 m^3) 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. When compared to fossil fuel generically states that carbon content is lower in 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, 22originated 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.

	Cellulose	**Hemicelluloses**	**Lignin**	**Extractives**
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
Fibre dimensions	**length, mm [aveg., (range)]**	**Diameter µm [aveg., (range)]**	**Fiber wall thickness(earlywood/late wood)**	**density [kg/m^3]**
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 is 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).

Component	Pine	Birch
Lignin	490	330
Carbohydrate derived		
- ***Hydroxy acids***	320	230
- ***Acetic acids***	50	120
- ***Formic acids***	80	50
Turpentine	10	–
Resin and/or fatty acids	50	40
Misch. products	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 Pine kraft black liquors dry solids typical distribution to organic chemical components and birch (Sjöström 1993, 158, Krotscheck&Sixta 2006, 968, Alén et al. 1992, 337, Alén1998)

fraction/component	**content (% of dry solids)** **Pinus sylvestris**	**content (% of dry solids)** **Betula pendula**
Lignin	46	38,0
Hydroxy acids		
Glycolic	3	2,8
Lactic	4,5	2,8
3,4-Dideoxypentonic	3	1,4
Glucoisosaccharinic	10,5	4,2
2-Hydroxybutonoic	1,5	7,0
3-Deoxypentonic	1,5	1,4
Xyloisosaccharinic	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 are 28 % form 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.

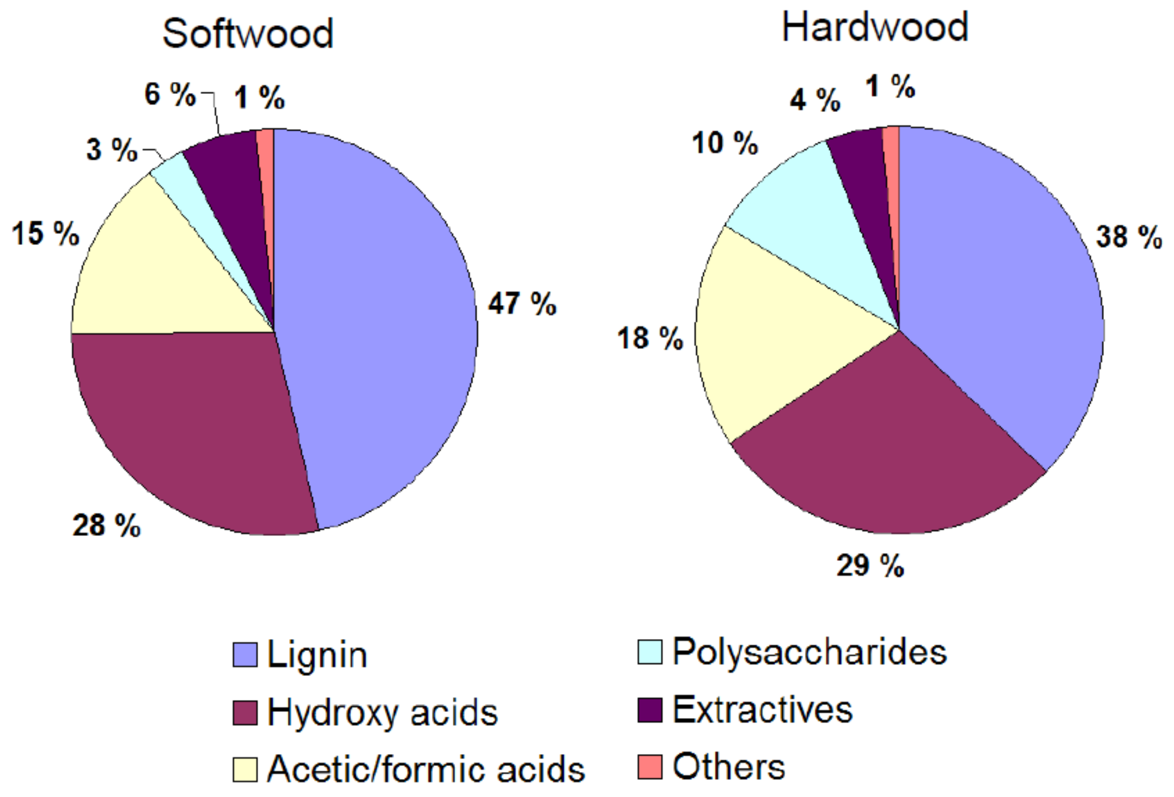
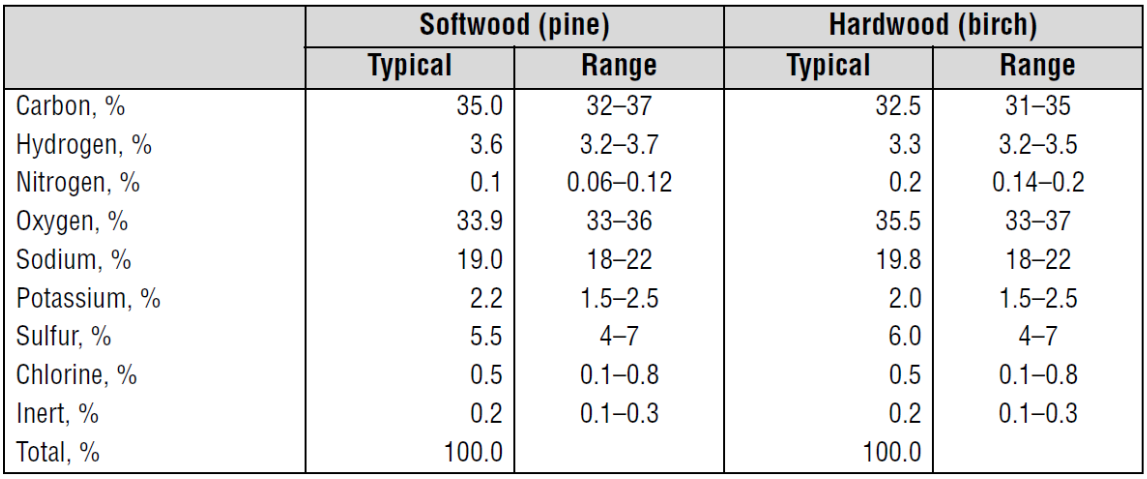


Figure 13 Diagram presenting distribution of black liquor organics, approximated (Niemelä et al. 2010).

As hard wood has different chemical composition than softwood species therefore compounds 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 chemical pulp produced contains after pulping 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 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 gas, which is a product flow, because of making wood based products. Calculations on combustion gas depend on the amount of black liquor to be burned and content of the black liquor, Section 2.3.

Certain terms are synonyms to each other; stack gas, flue gas, exit gas, combustion gas and chimney gas. In here all mean similar gaseous emissions exiting stack to the surrounding atmosphere. Special attention from the public and thereby from industry needs to be added to these air emissions. Monitoring is a key in industrial air pollution control and measurement. In Finland, forest industry spent quite an amount in environmental protection. Since year 2007 to 2016 on average 150 million euros was spent per year to the environmental protection technologies and maintenance. Figure 14 present 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.

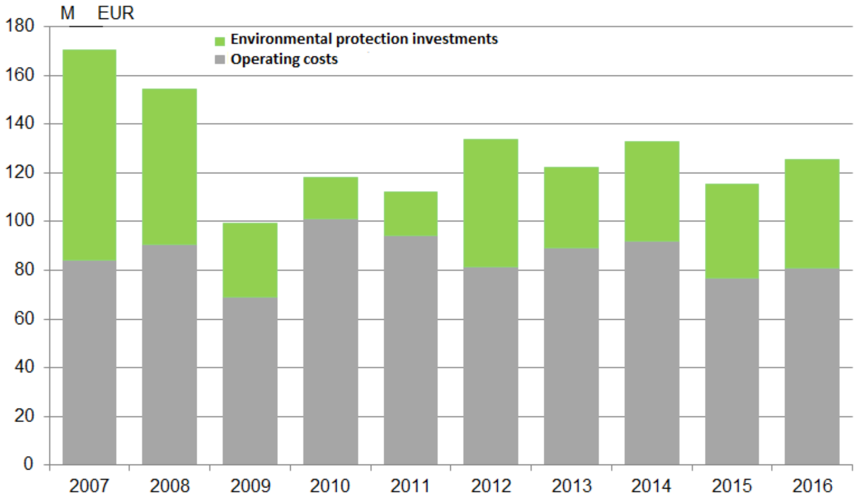


Figure 14 Forest industry Finland spends continually money to environmental protection on its mills and other related activities. (Finnish Forest Industries 2017).

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 theses 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 years 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.

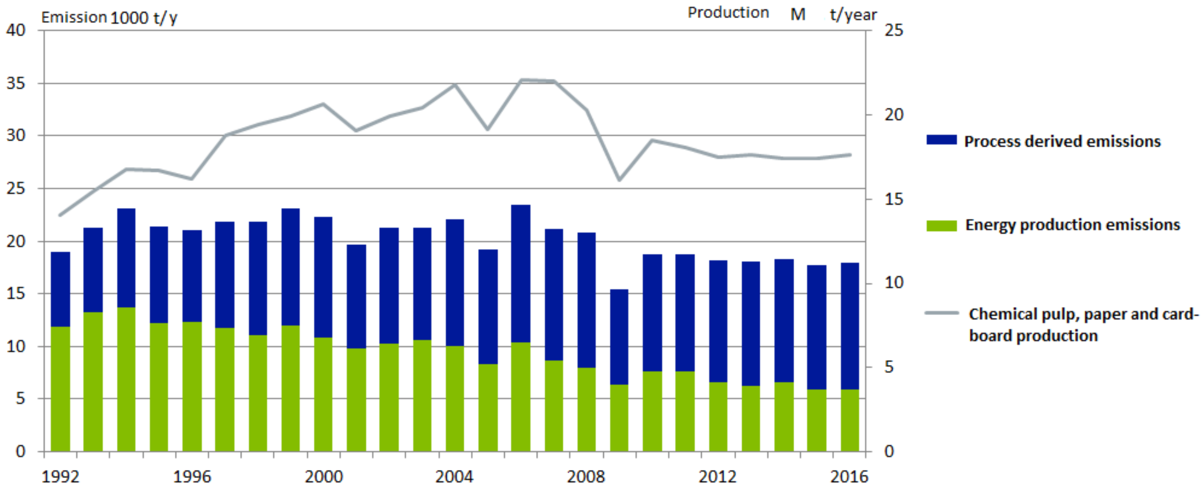


Figure 15 Nitrogen oxide emissions yearly 1992 – 2016. (Finnish Forest Industries 2017).

Nitrogen oxides did not have 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.

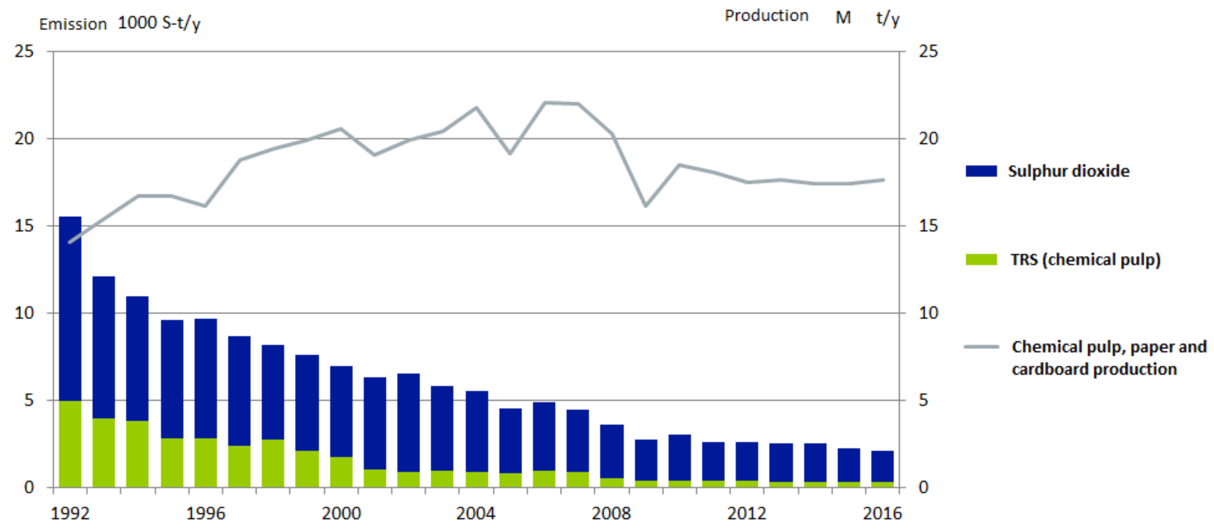


Figure 16 Sulphur gaseous emissions have been successfully reduced during the years. (Finnish Forest Industries 2017)

In figure 16 are sulphur gaseous emissions during last years of operation in forest industries. Sulphurous emissions have been reduced significantly from the past. Especially TRS that is related strongly to odours is 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 electrostatic precipitator.

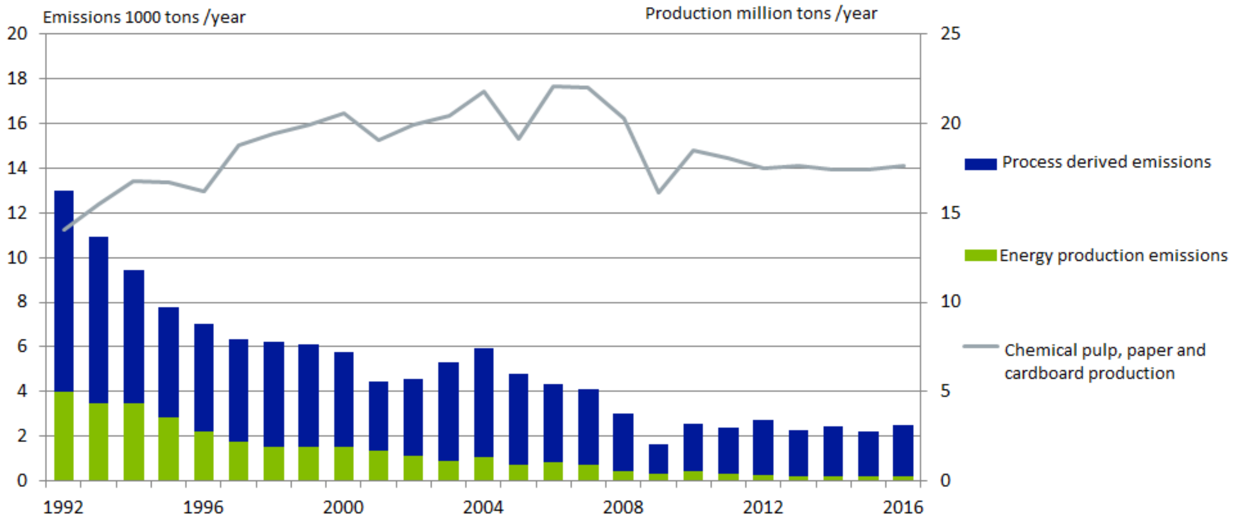


Figure 17 Emission of particulate matter in the Finnish forest industry years 1992 – 2016. (Finnish Forest Industries. 2017)

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 economical boost to the economy. To remind recovery system the main processes in recovery cycle are evaporating black liquor (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 effective reduction of both TRS and SO_2 emissions in to fire black liquor in a higher dry solids content. Comparing this to the CNCG plus the fuel oil burned is more significant source of SO_2. SO_2 is formed in mainly through oxidation of H_2S and carbonyl sulphide in lower furnace. Black liquor is the major source for this. Higher dry solids content makes higher temperature, air is supplied and mixed well with fuel, where emissions are lower.

Nitrogen oxides NOx 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^3 (BREF PP 2015 795). Increased dry solids content of the black liquor has increased proportional NOx concentration in the flue gases.

Bioenergy is at the moment 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 loss. Exit gases that leave the stack to the atmosphere are not utilized by anyone. Heat and power generation using biomass is part of biorefinerys working environment.

Kraft mills use 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 lime kiln, white liquor preparation (causticizing), bark combustion facilities, evaporator, cooking and washing. Overview to forest industries whole processes and chemistry and physics can be found from *Bajpai* 2010, Papermaking science and technology book series and *Handbook of Pulp*. edited by Herbert Sixta. A large bibliography is dedicated for chemical pulp making only. Figure 18 represents general cycle of kraft recovery cycle.

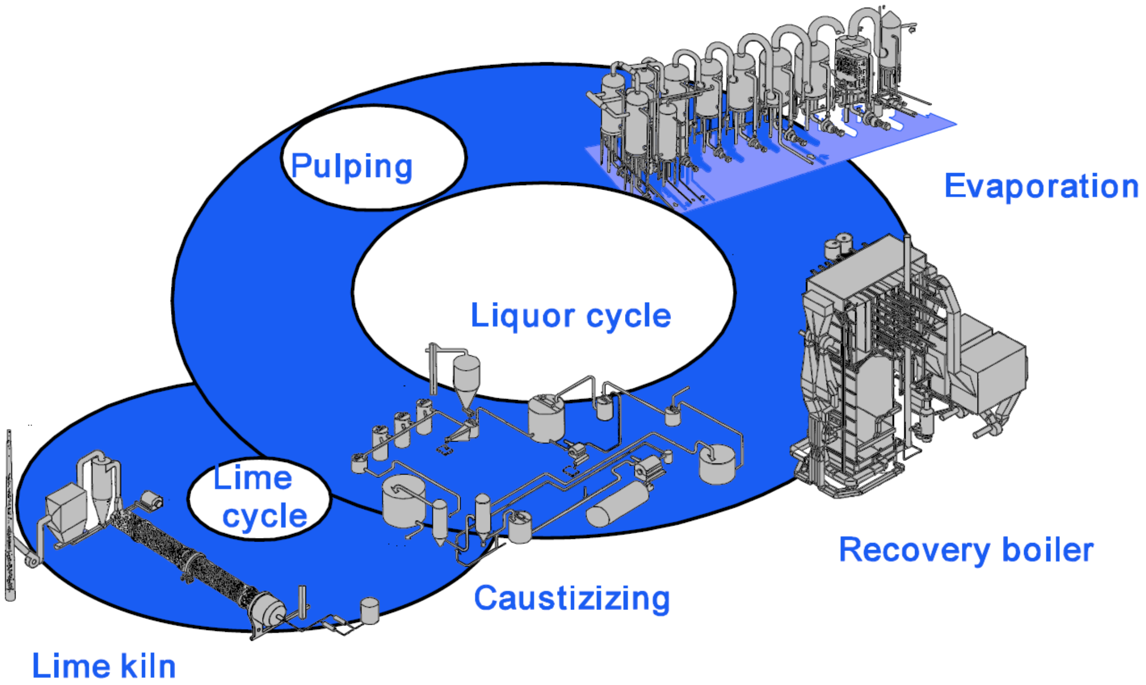


Figure 18 Cycles of kraft recovery (Kivistö&Vakkilainen 2010, 58)

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 in making of chemical pulp. On every mill has certain own steps in fibre line as well in the chemical recovery. Data on black liquor quality and smelt can be obtained through analyses.

Pulp has reputation of bad odour releases by the public. The odour is caused by some of the sulphur contaning 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).

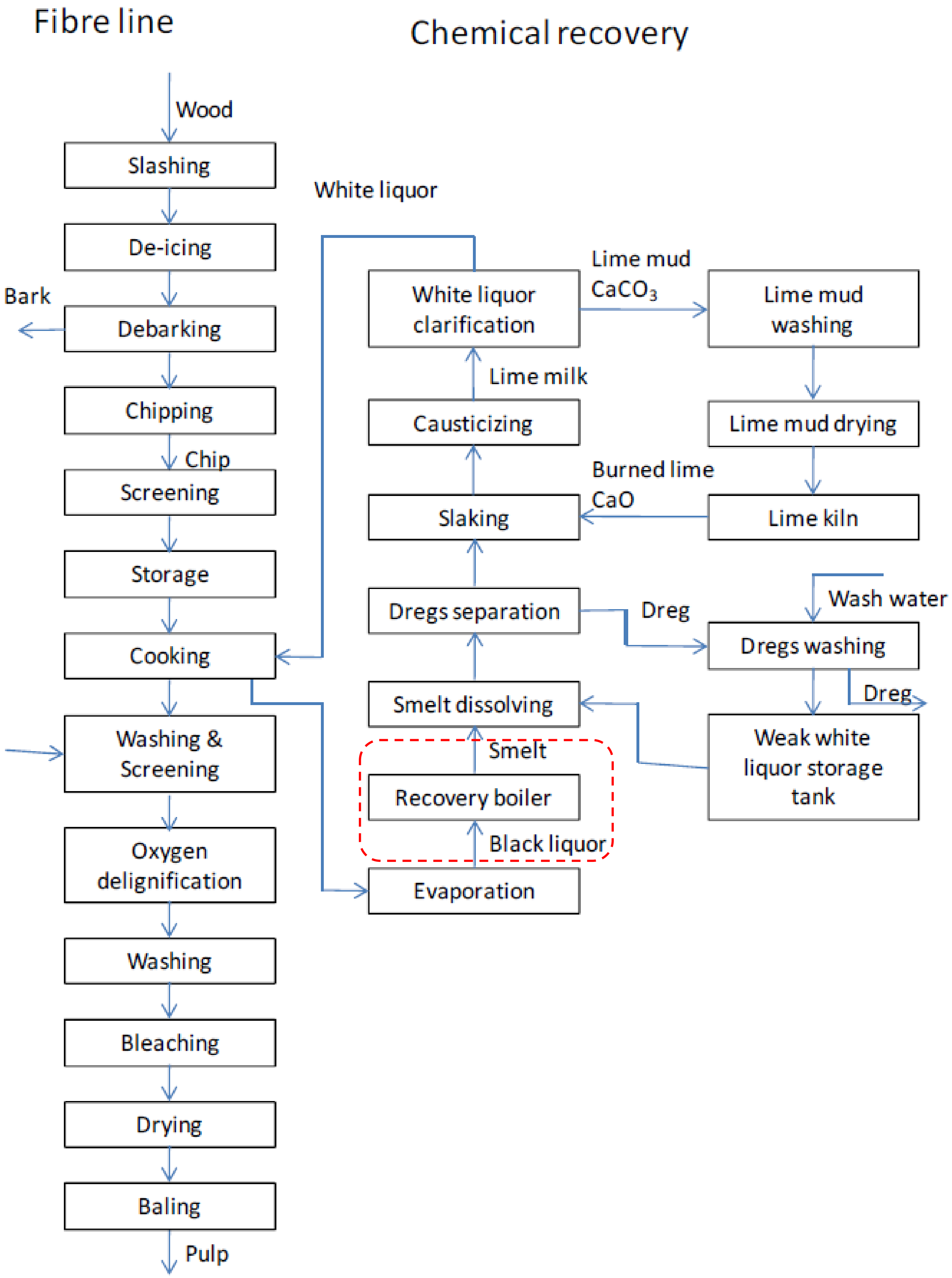


Figure 19 The chemical pulping process and RB placement in red. In the courtesy of (Kivistö&Vakkilainen 2010, 33)

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 significant role in 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 (Na_2S) and sodium carbonate (Na_2CO_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. NaS_2 and 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 Nm^3/ADt lime kiln has values of 303 – 1000 Nm^3 /ADt (not reported in same reference oxygen level). Given values from officials should be correct. We may use produced mass of pulp, which should not be muddled with the capacity of pulp production a given year. Production is either lower than capacity or higher than assumed. Annual emitted masses of NO_x, ash and SO_2 are obtained statistically. 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.

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 can effect to the result of NO_x emissions per tonne also specific water borne emissions are lower. It could be said that lower the yield higher the specific emissions.

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 also influence to the level of closure in water system in the mill and amount of the bio sludge. As well as recovery units own operation combustion properties and water content of black liquor. Biological treatment at 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)

Should it 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 is 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 certain point, where running combustion is better for many reasons. If overloading occurs SO_2 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 be future by increasing mass and sort 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 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 environmental chiefs of the company, they have to conclude 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 a technical devices and methods are scrubbers, boilers burn control and those multiple usually simultaneous impacts of the direct measurement.

Industrial emissions directive 2010/75/EU is one directive inside EU that does make RB’s operation lawful operative process boiler.

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 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 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 on 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 $kg_{pollutant}$/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 mg/m^3n for certain pollutant again typically as annual average. Flue gas flow per air-dry ton of chemical pulp (Nm^3/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 (ROM. 2018, 63).

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

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 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.

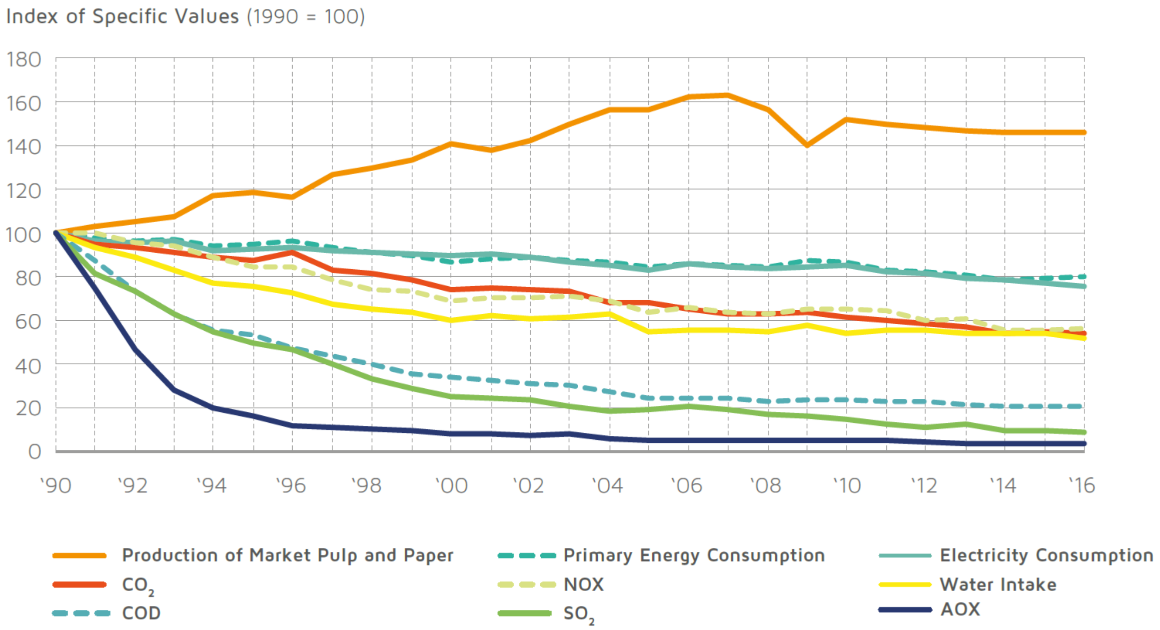


Figure 20 Evolution of Environmental Impacts of the CEPI Pulp and Paper Industry

Coming towards 2020 it should recognized that more suitable balancing year for such diagrams as figure 20 could be from 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 parameter for matter of this thesis, Nm^3/ ton of produced dry pulp, 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 emissions to atmosphere, 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)

Daily average	Average over a period of 24 hours based on valid hourly averages from continuous measurement
Average over the sampling period	Average value of three consecutive measurements of at least 30 minutes each
Yearly average	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 is interesting, two different cases apply in case of 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 mg/m^{3}n is value. These values should be referred that they are in standard condition (refer to Nm^3 or m^{3}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 be always notified. RB in Finland has reference oxygen of 6%. Equation 2 presents way of changing concentrations from measured oxygen level to another. (BREF PP 2015, 58)

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

where E_r emission concentration in reference state (mg/m^{3}n)

O_r is reference oxygen level (vol-%)

E_m is emissions concentration in measured oxygen (mg/m^{3}n)

O_m is measured oxygen level in RB duct (vol-%)

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

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

where V_r is standard condition volumetric flue gas in reference oxygen (Nm^3)

V_m is standard condition volumetric flue gas amount in measured oxygen content, real excess oxygen in % during operation (Nm^3)

As can be seen in equation 3 if reference oxygen content is higher than the measured content volume raises, when reporting flue gas flows in reference oxygen state. 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^3 to kg/ADt.

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

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

The calculation of specific loads need the following initial data.

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

Often mills report emissions they are guided to present 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)

4.1.3 Continuous measurement and periodical measurements

Relevant parameters for 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 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 result of two things, 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 mathematical model (C,H,O,N,S, ash, moisture and energy content are used as data input), Appendix II contains example of 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, continously monitored, periodical measurement
SO_2	continously monitored, periodical measurement
TRS or H_2S	continously monitored, periodical measurement
NO_x	continously 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)

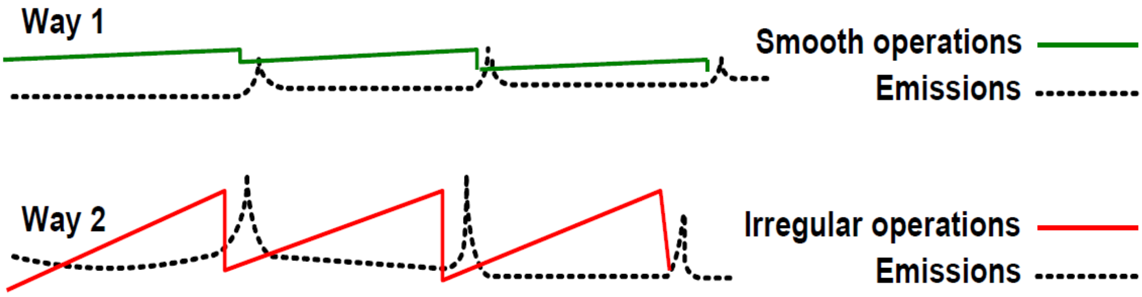


Figure 21 Emission levels depend on how mill is operated (Nilsson et al. 2007, 16).

Advices for way 1 mill in figure 21 operation are given such points:

- Computer-based control systems with on-line measurements in monitoring of atmospheric emissions reduces the need for separate emission control, and additionally enables statistical follow-up. Information and automation are there.
- Monitoring of process parameters with continuous measurements demonstrate stability of both manufacturing processes and emission control techniques, allows data to operate close to the optimum process parameters and stabilizing critical process parameters 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)

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; 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. Tertiary burner burns gases fully. Flue ash contains unburned materials. Boiler efficiency and burn control is closely related to Subsection 3.2.3.

Modern latest year RB’s work in area of 3200 – 5000 tds/day (Jinhai pulp and paper in Hainan, China 7000 tsd/day and produces steam 510℃ 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 example there must be a place to measure. Table 12 summarizes certain challenges to their contents.

When 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 to obtain trustworthy results.

Table 12 Instrumentation problem associated with emissions measurement in stationary sources

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

4.2 Measurement technologies and emission measurement devices

It is mandatory 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. Branch of industrial emission monitoring and reporting is quite new, as it 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 standards are closer to European standards and use definitely more precise methods. Measurement becomes more complicated. Older methods have attained proven status as deflects are better understood than those of new technologies, but real-time and continuous measurement might be less affordable in case of older methods. In United States is used EPA methods. Environmental equipment is a part of purchase of RB, significant increase in instrumentation markets in continuous emissions measurement is due to legal binding that GHG should be accounted as 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 recovery ash build up on surface of measuring devices and flue gas moisture (Subsection 3.2.3).

4.2.1 Ultrasonic gas flow rate measurer

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

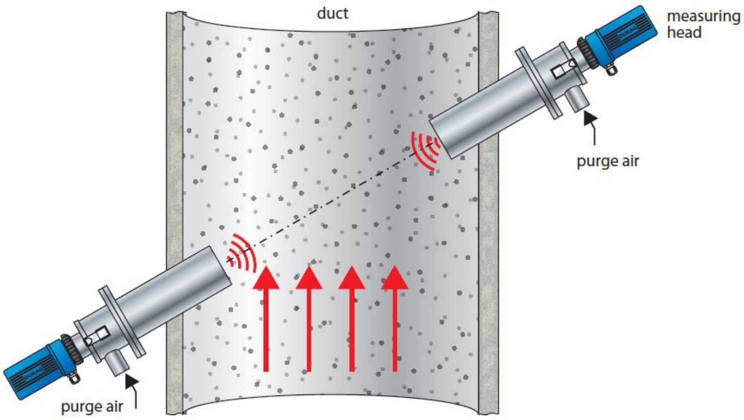


Figure 22 Durag D-FL 220 operating principle (Durag 2018)

4.2.2 Thermal mass flow measurement sensors

In RB’s exit gases temperatures are usually higher and contains 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 have good accuracy (1-2 % uncertainty).

4.2.3 Integrating pitot-tube

Stack can be instrumented with averaging Pitot tube. Pitot tube is in principal a differentiating pressure measurement. Integrating Pitot tube is 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

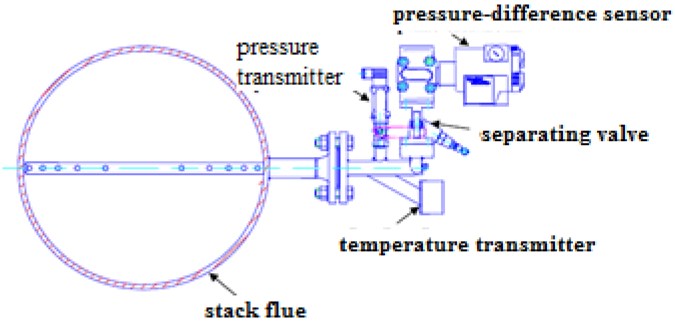


Figure 23 Example of integrating Pitot tube (Adapted from Kontram)

4.2.4 Multi-gas concentration measurer

Fourier Transform Infrared FTIR is 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 power plant.

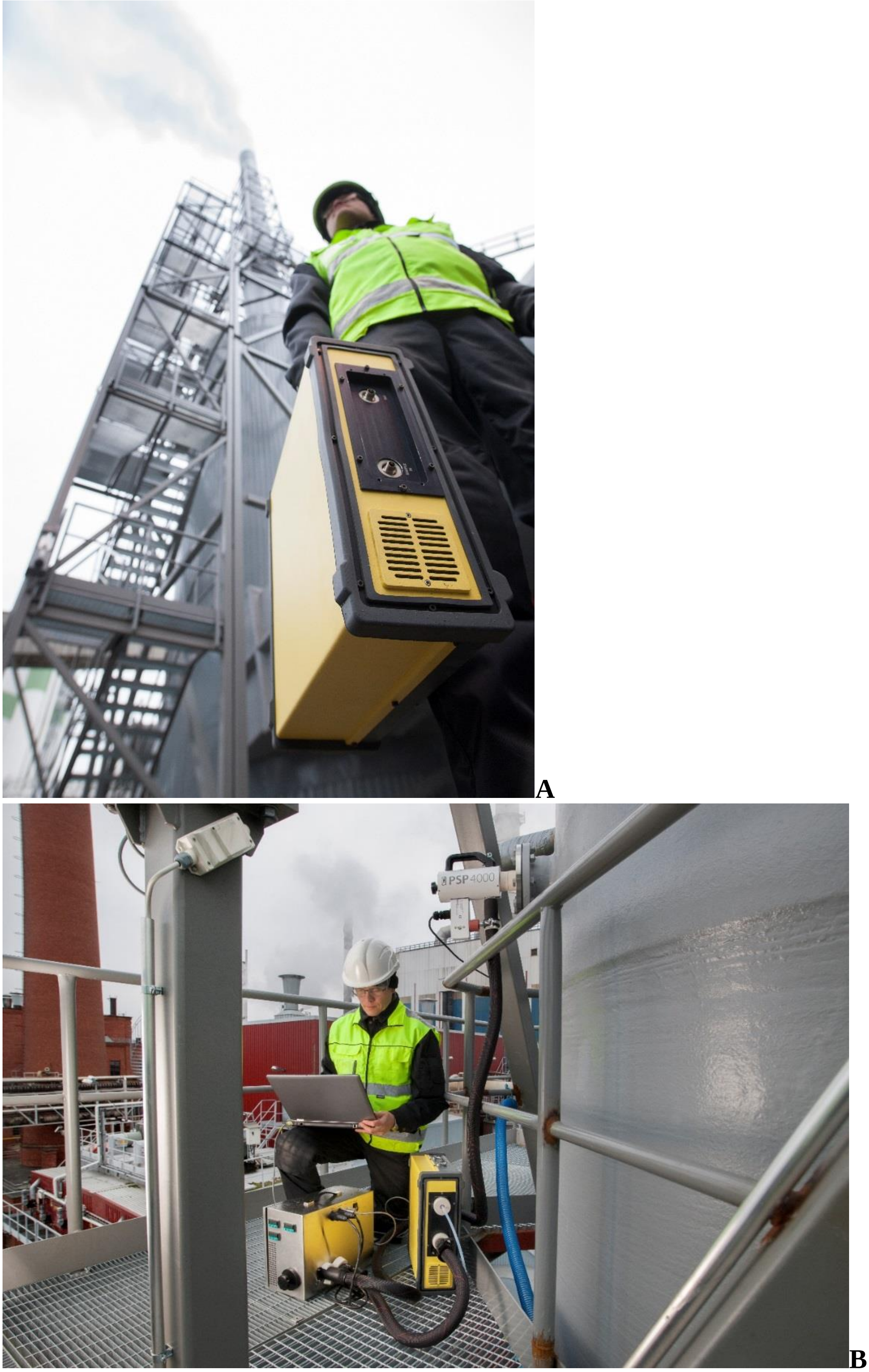


Figure 24 Above pictures A and B show how measurer works with the FTIR in some industrial flue gas (pictures from Gasmet Oy)

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 provide also the white paper for FTIR measurer to give the principles and overview to FTIR technology (Gasmet 2018).

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

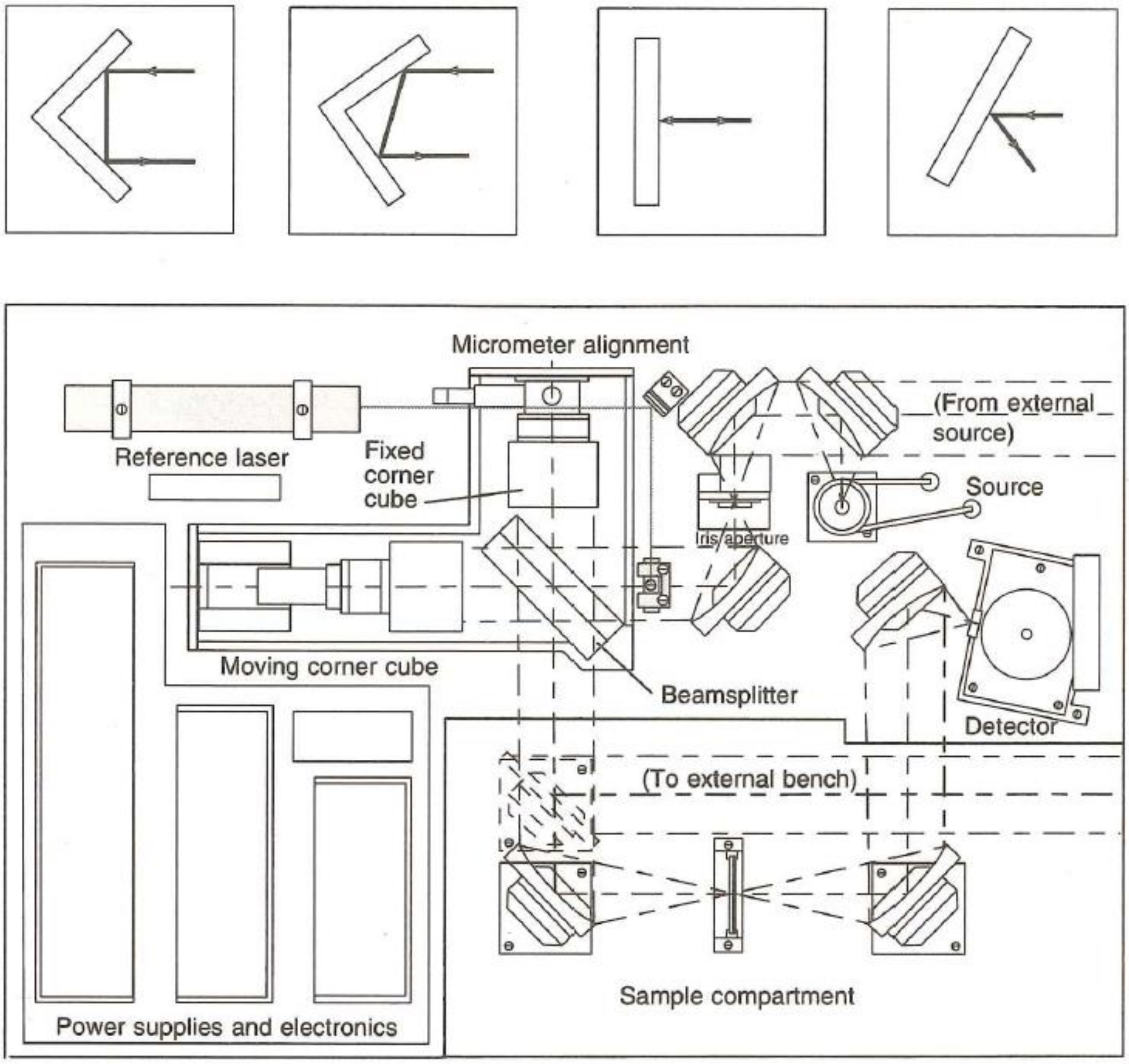


Figure 25 Construction of FTIR device for measurement (Torvela. 1994, 123)

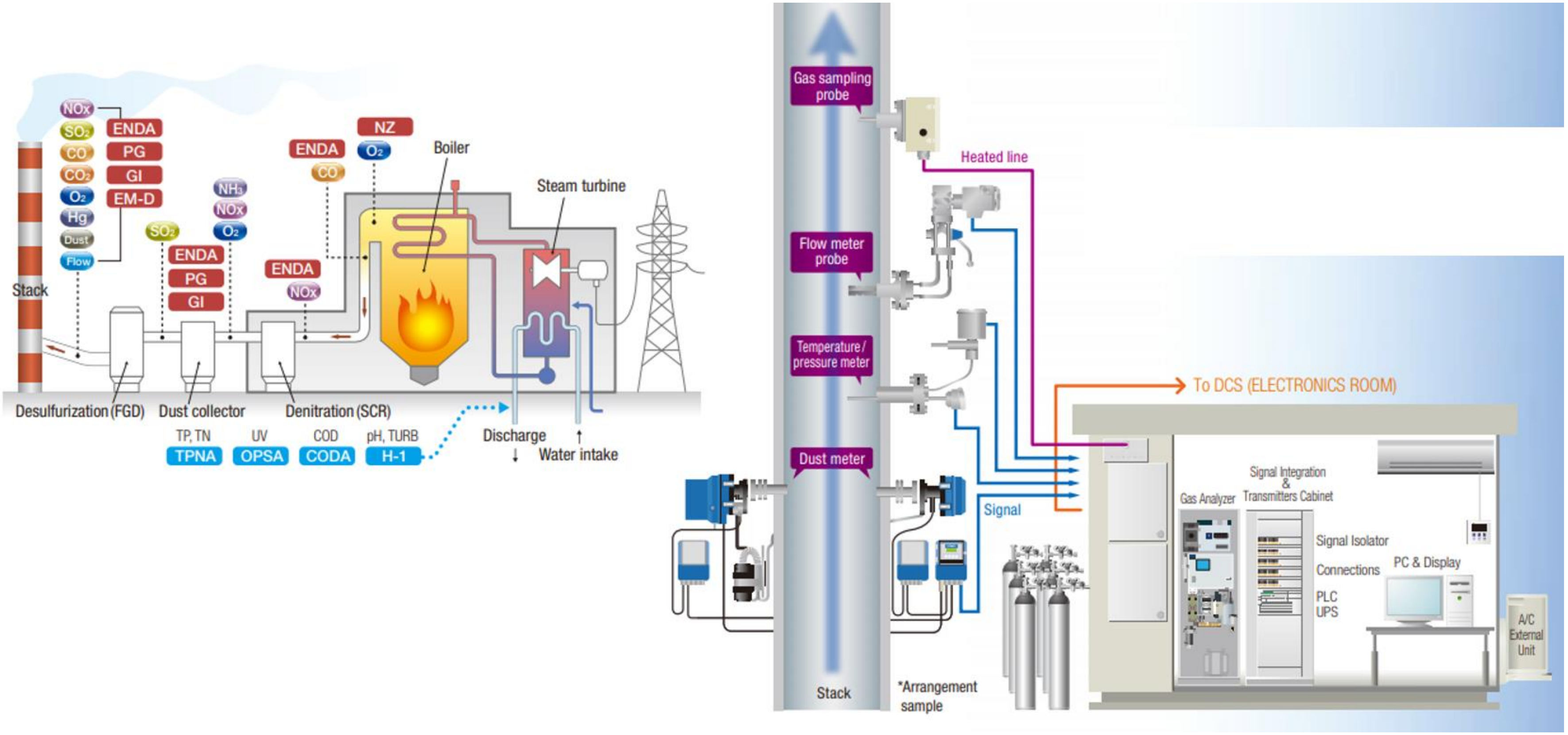


Figure 26 Continuous emissions measurement procedures and example of all the components in industrial boilers

4.3 Volume rate in duct – flue gas flow

First shall be verified a bit of the nature of the flue gas flow. Seemingly variation on flue gas flow is 6000 – 9000 Nm^3/ADt (Dahl 2008, 125), depending on wood species 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 concentration 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 trace gas system, energy-mass balance computation. Still many prefer Pitot – tube, which measures velocity of the flue gas. Pressure sensing methods are using following equation 4.

$$q_v = A\bar{v} \tag{4}$$

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 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 example of boundary of emission balance might be 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 in 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.

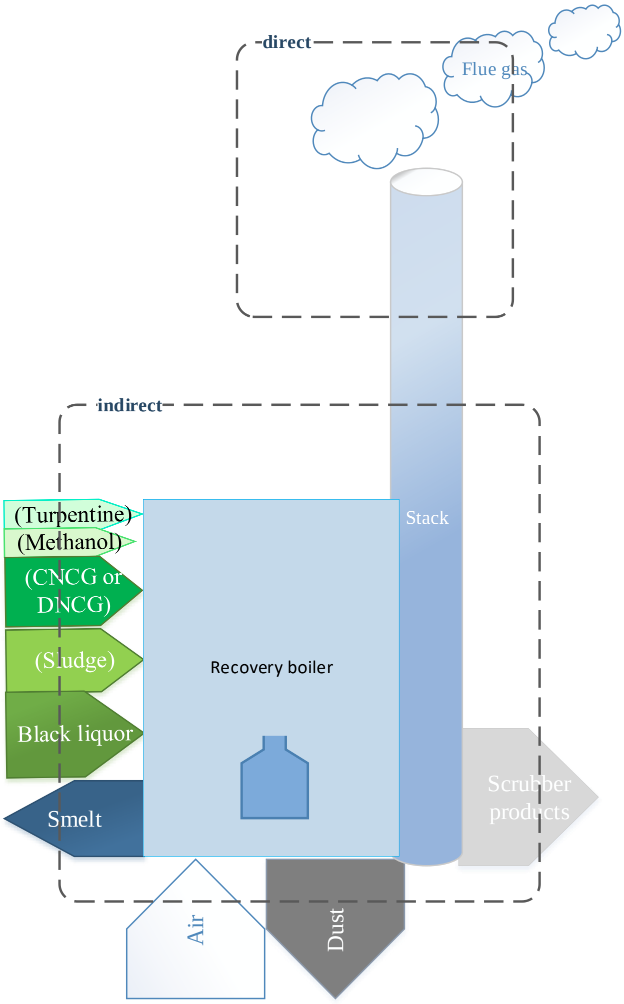


Figure 27 Examples of boundaries in RB to environment and emissions measurement – direct and indirect method for flue gas flow

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 measurement of 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 amounts of the flue gas is black liquor combustion calculation averaged to the year (Jussila 2007).

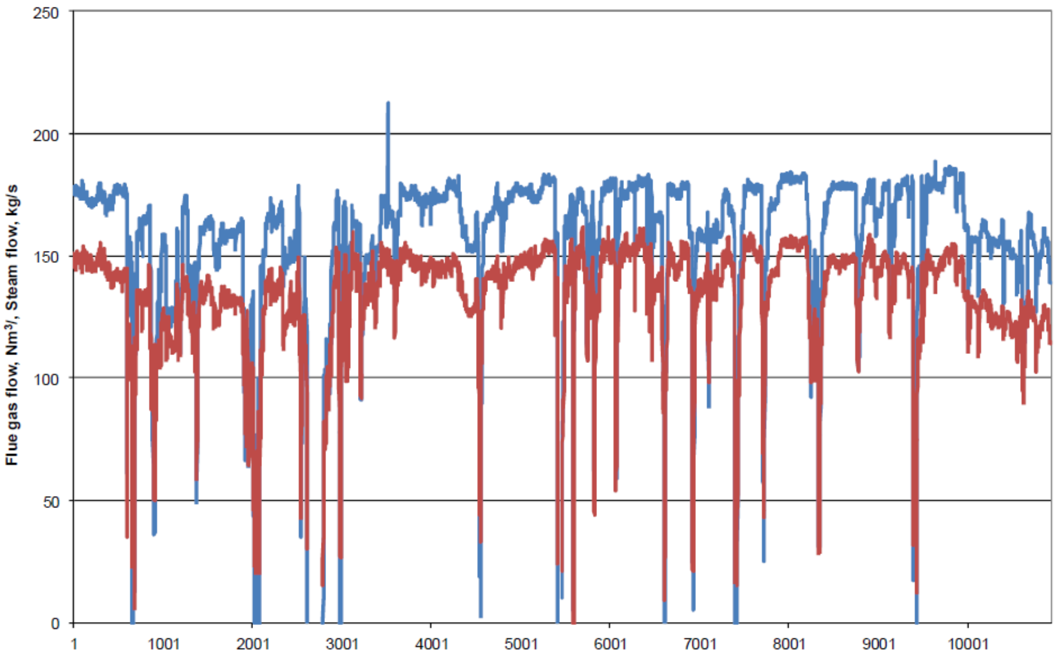


Figure 28 RB steam and flue gas flow (hourly averages) as example of flow rate changes. Red one is the steam (kg/s) and the blue line is flue gas flow (Nm^3/s) (Hamaguchi&Vakkilainen 2010, 29).

Faults may cause shut down of 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^3/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.

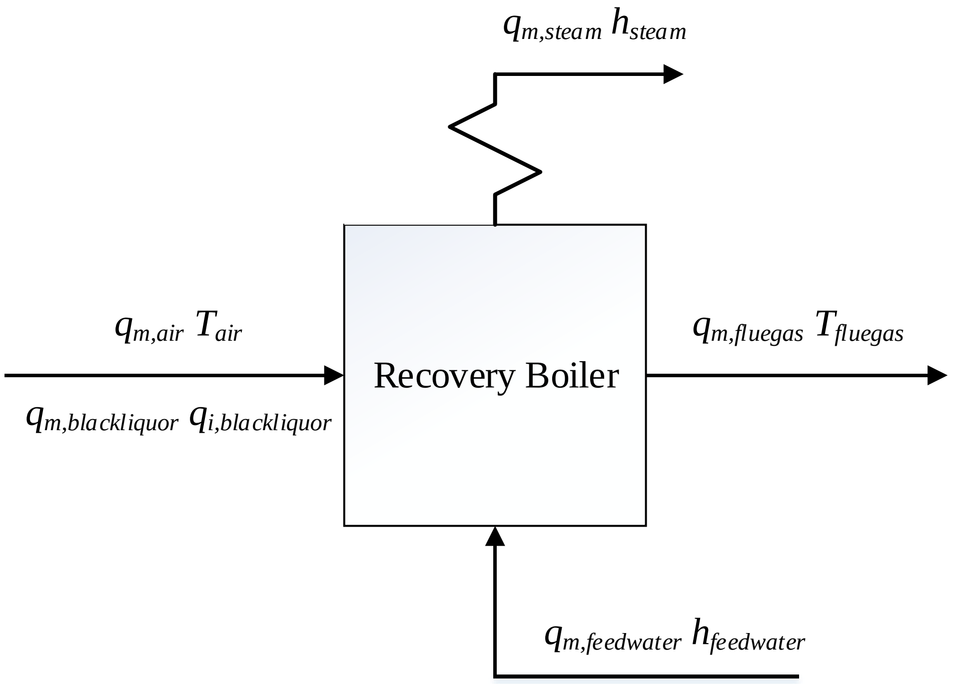


Figure 29 RB power – and mass balance. (Hammo 2000, 6)

Energy balance is

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

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^3n.

When reporting annual total mass of compound, which were discharged to 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_2, NO, SO_2, SO_3, sulphuric acid aerosols, methyl mercaptans, H_2S, CO_2, C_xH_y, CO, H_2O, O_2, N_2, ash, heavy metals, gaseous chlorides HCL – equivalents, Hg, NH_3, Gaseous fluorides HF–equivalents, VOC, total gaseous organic carbon TVOC, PCDDs/PCDFs and dioxin-like PCBs (JRC 2017, 34).

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

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 example 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, 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 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 predetermined. 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 presented collected name of analytical method and its component to meter. Some of the methods work in continuous and some in batch. In table 13 is presented certain type of methods of testing different gas components. IR is infrared and UV ultraviolet light. Industry is using in continuous metering multicomponent measurer nowadays as there have been great leap in development such devise in recent years.

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

Measurement	technique	method	technique
O_2	zirconia probe	paramagnetism	
CO	IR	catalytic oxidation	
CO_2	IR		
SO_2	IR	UV	UV-fluorescence
NO_x (=NO_2+NO)	IR	UV	chemiluminescence
particle emissions	Optical (filament lamp)	Optical (laser)	piezoelectric sensor

Table 14 Measurement analytical method, targeted component.

Analytical principles	**Target component**	**Continuous or batch**	**Remarks**
Non-Dispersive Infrared (NDIR) absorption detection	CO, CO_2	Continuous	
	NO	Continuous	
	N2O	Continuous	
	HC	Continuous	As "n-C6H14 equivalent"
Flame ionization detection (FID)	Total hydrocarbons	Continuous	
	CH4, Non-Methane Hydrocarbons (NMHC)	Continuous or batch	In combination with NMC or GC
Chemiluminescence Detection	NO, NO2, NOx, (NO + NO2)	Continuous	
Non-Dispersive Ultraviolet (NDUV) detection	NOx (NO + NO2)	Continuous	
Paramagnetic Detection (PMD)	O2	Continuous	
Zirconia solid electrolyte method	O2, NOx, Air-to-fuel ratio	Continuous	In-situ measurement (non-sampling)
Fourier Transform Infrared (FTIR) spectroscopy	N2O NH3 CO, CO2, NO, H2O, NO2, C2H5OH, HCHO, CH4, et cetera	Continuous	Simultaneous, multicomponent analysis
Quantum Cascade Laser Infrared (QCL-IR) Spectroscopy	NO, NO2, N2O, NH3	Continuous	Simultaneous, multicomponent analysis
Gas Chromatography	Hydrocarbons or methane	Batch	
	Alcohols	Batch	
	N2O	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 *Aumala* (2000).

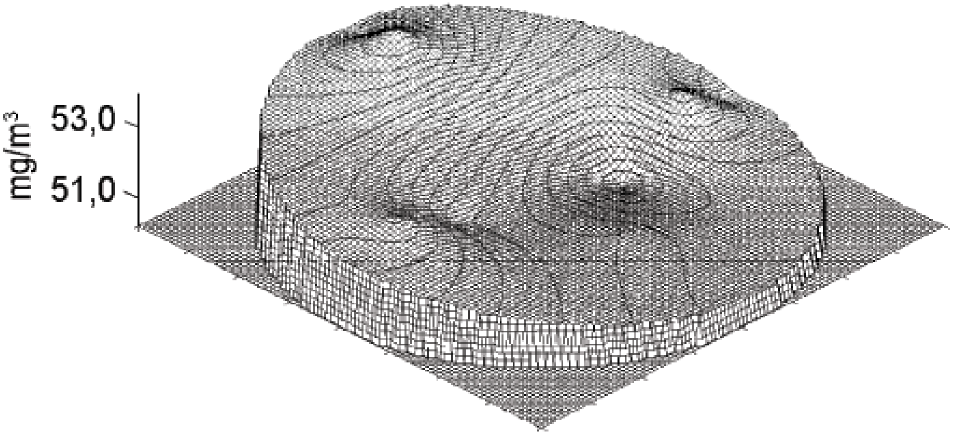
Table 15 Flue gas components (Aumala 2000, 323).

Gas component	Purpose of measurement	Measuring necessity
O_2	control	continuous
CO	control, emission	continuous
CO_2	control, emission	continuous
SO_2	control, emission	continuous/ temporary
NO (=NO_2+NO)	emission	continuous/ temporary
H_2S	emission	continuous/ temporary
particle emissions	emission	continuous/ temporary
heavy metals	emission	continuous/ temporary

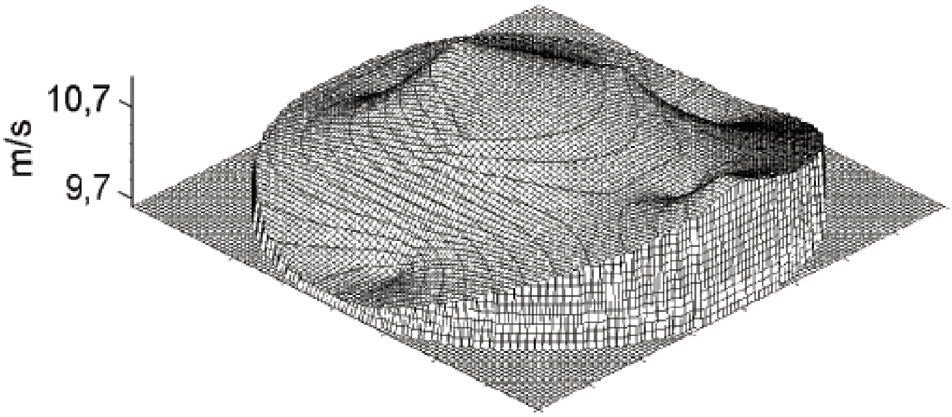
4.3.6 Flow profile

Flow measurement needs to be symmetrical to calculate the real value exact. Symmetrical flow means there is certain symmetricity in the gaseous flow in the pipe. Waste gas profiles are better to be homogenous than inhomogeneous. Figure 30 presents 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).

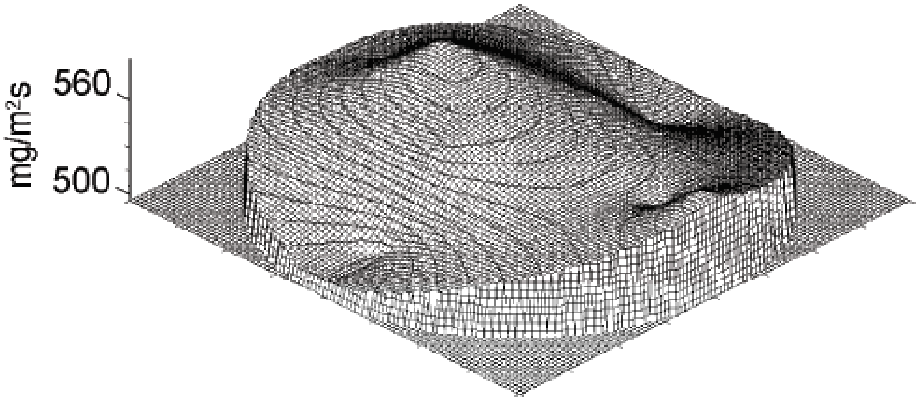
As seen in figure 30 velocities are very different in other side of the channel than other. Mills environmental staff often calculates or estimates flows and measurement is not option due to this. In Section 4.2 shortly described one optional mass flow meter, one should still remember possibility of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



Mass concentration

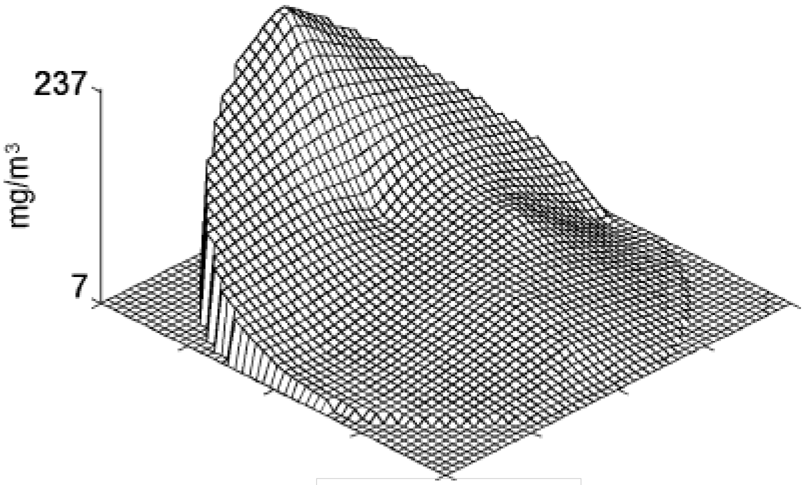


Velocity

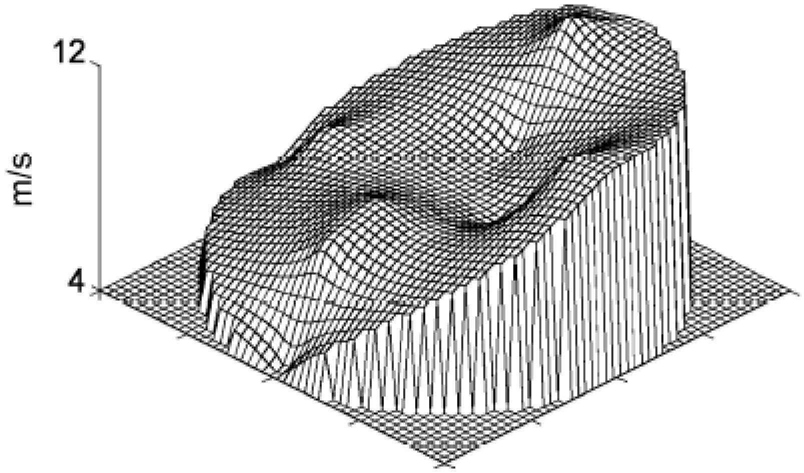


Mass flow density

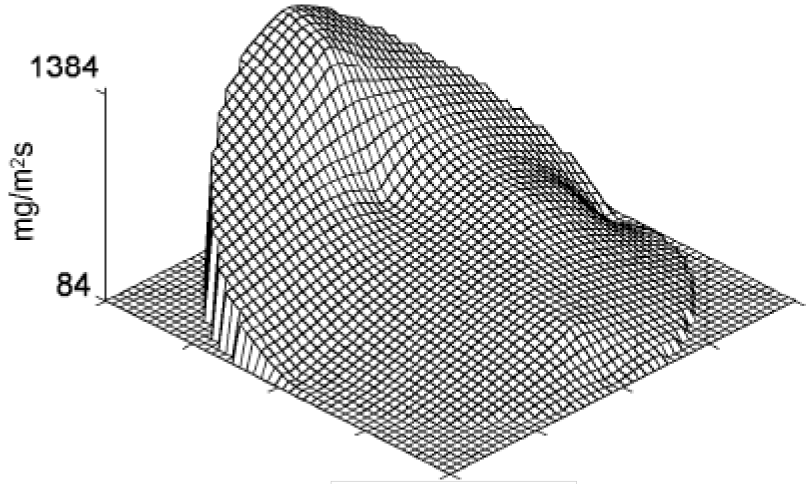
Figure 30 Example of one component (organic gaseous substance, propane) and its homogenous measurement plane



Mass concentration



Velocity



Mass flow density

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

5 RESULTS

As at 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 the 16 operating boilers (EIPPCB 2008). Two mills have two separate RBs, so 14 columns of boilers in the tables below.

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

5.1 RBs in Finland – data

Table 16 presents years 2016 emissions in mass. Pulp production total emissions are direct air emissions. Energy production emissions are from other than RB. Mass of NO_x emissions are the largest in every mill compared to TRS, SO_2 or particulates.

In table 17 are presented year 2016 produced pulp in tons. and respect to that modelled value of specific NO_x emission. Lime kiln specific emissions and odor gas flare specific emissions were from 2008, while newer information was not available. It is assumed as good estimate to year 2016. In table 17 year 2016 specific model for NO_x is some different than reported for year 2008. Following then model flue gas flows, calculation sample for hardwood and softwood is in Appendix II. In table 18 %-of wood used is assumed to be mass percent. Process oxygen is in the model 3 % and reference oxygen content is 6 %. Comparable flue gas flows are in the last column for every RB. Mills using hardwood are having smaller flue gas flows than fully softwood using mills. Yield chosen for the mill changes result greatly.

Table 19 is the flue gas table where we can see certain differences. Mill G and L have significantly smaller flow per ton than model of combustion delivered. Also Mill C, E and M produces in 400 – 600 Nm^3 difference to modelled values.

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_2, t(SO_2)	TRS, t(S)	NOx, t(NO_2)	Particulates, t	SO_2, t(SO_2)	NOx, t(NO_2)	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	
Milll 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 kg/ADt	Lime kiln NOx* kg/ADt	Odor gases flare NOx* kg/ADt	Recovery boiler NOx * kg/ADt	**Reported for RB** kg/ADt
Mill A	**200 000**	0,91			**0,91**	**1,75**
Mill B	**618 700**	1,37	0,21		**1,16**	**1,22**
Mill C	**603 524**	1,72	0,23		**1,49**	**1,85**
Mill D	**585 187**	1,49	0,27		**1,22**	**1,42**
Mill E	**509 962**	1,85	0,36	0,050	**1,44**	**1,20**
Mill F	**460 000**	1,70	0,14	0,200	**1,36**	**1,13**
Mill G*	**1 126 000**	1,47	0,13	0,100	**1,24**	**1,26**
Mill H	**349 000**	2,16	0,34		**1,82**	**1,35**
Mill I*	**371 000**	1,71	0,24	0,040	**1,43**	**1,58**
Mill J	**305 000**	1,14	0,52		**0,62**	**1,63**
Mill K	**429 000**	1,29	0,19		**1,10**	**2,01**
Mill L	**655 000**	1,50	0,33	0,220	**0,95**	**1,36**
Milll M	**775 000**	1,56	0,05	0,180	**1,33**	**1,43**
Mill N	**782 000**	1,49	0,05	0,001	**1,43**	**1,05**
*two RBs in mill			*2008 questionaire EIPPC	*2008 questionaire EIPPC	*2008 questionaire 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.

			softwood					hardwood					
	%- of wood used		m^3n/Adt*	%	m^3n/Adt	m^3n/s	m3n/s	m^3n/Adt	%	m^3n/ADt	m^3n/s	m^3n/s	m^3n/Adt
	softwood	hardwood	wet process O_2	Yield used*	dry 6% O_2	wet, [process 3%O_2	dry, [process 3%O_2]	wet real O_2	Yield used	dry 6% O_2	wet, [O2-content]	dry, [process 3% O	dry, 6% ref O_2
Mill A	**100**	**0**	7 768	46	8 236	51	45	-	-	-	-	-	**8 236**
Mill B	**100**	**0**		43	9 114	174	153	-	-	-	-	-	**9 114**
Mill C	**65**	**35**		46	8 236		91		49	6 828		34	**7 743**
Mill D	**100**	**0**	8 309	44	8 808	106	94	-	-	-	-	-	**8 808**
Mill E	**44**	**56**	8 033	45	8 515	59	52	6 706	49	6 828	62	53	**7 571**
Mill F	**62**	**38**	7 928	46	8 236	74	64	6627	49	6 828	28	24	**7 701**
Mill G	**45**	**55**	8 203	45	8 515	136	117	6 857	48	7 060	138	119	**7 715**
Mill H	**100**	**0**	8 014	46	8236	91	78	-	-	-	-	-	**8 236**
Mill I	**100**	**0**	8 309	44	8 808	101	89	-	-	-	-	-	**8 808**
Mill J	**60**	**40**	8 151	45	8 515	48,63	42	7 043	47	7 301	28	24	**8 030**
Mill K	**35**	**65**	8 309	44	8 808	41	36	6 996	47	7 301	64	55	**7 829**
Mill L	**60**	**40**	7 640	46,5	8 101	98	86	6 521	49	6 828	56	49	**7 592**
Mill M	**38**	**62**	7 768	46	8 236	75	66	6 442	49	6 828	101	89	**7 363**
Mill N	**52**	**48**	8 552	44	9 114	113	101	7 127	46	7 553	87	77	**8 365**

* 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. Estimating conjecture was made by thesis worker.

	Model of combustion results m^3n/Adt dry, 6-% ref O_2	**Reported (O2-level process dependent)** Volumetric flow rate Nm^3/ADt, stand. cond., dry gas	**Converted to the same ref. O_2-level from reported** Volumetric flow rate Nm^3/ADt, stand. cond., dry gas (6%)	**Conjecture made by thesis worker from reported value** Volumetric flow rate Nm^3/ADt, stand. cond., dry gas (6%)
Mill A	**8 236**	**-**	**-**	-
Mill B	**9 114**	**8 250**	**9 900**	-
Mill C	**7 743**	**7 356**	**7 356**	7 341
Mill D	**8 808**	**7 630**	**8 902**	-
Mill E	**7 571**	**7 128**	**7 128**	7 603
Mill F	**7 701**	**7 600**	**9 000**	8 610
Mill G	**7 715**	**5 800**	**5 800**	-
Mill H	**8 236**	**7 250**	**8 410**	-
Mill I*	**8 808**	**10 491**	**9246 / 10673**	10 078
Mill J	**8 030**	**8 069**	**8 069**	-
Mill K	**7 829**	**7 600**	**8 107**	-
Mill L	**7 592**	**6 800**	**6 845**	7 782
Mill M	**7 363**	**6 642**	**6 775**	7 730
Mill N	**8 365**	**7 400**	**8 387**	-

* 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_x.

	Model of combustion flow and NO_x concentrations		Modelled Nm3/ADt to reported kg/ADt Nox (2008)
	m^3n/s dry, process 3 % O_2	mg NO_2/m^3n (kg/ADt 2016) dry, 6% ref O_2	mg NO_2/m^3n dry, 6% ref O_2
Mill A	**45**	110	**-**
Mill B	**153**	127	**134**
Mill C	**125**	193	**239**
Mill D	**94**	138	**161**
Mill E	**105**	190	**159**
Mill F	**88**	177	**147**
Mill G	**236**	161	**163**
Mill H	**78**	221	**164**
Mill I	**89**	162	**179**
Mill J	**67**	77	**203**
Mill K	**91**	141	**257**
Mill L	**135**	126	**179**
Mill M	**155**	180	**194**
Mill N	**178**	172	**126**

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_2/m^3n dry, 6% ref O_2	Reported flue gas to reported Nox (2008) mg NO_2/m^3n dry, 6% ref O_2	Conjecture flue gas to 2016 NOx kg/ADt mg NO_2/m^3n dry, 6% ref O_2	Conjecture and reported 2008 mg NO_2/m^3n dry, 6% ref O_2	**Reported EIPPC concentration** mg NO_2/m^3n dry, O_2 varying reported differently	**Reported** mg NO_2/m^3n dry, 6% ref O_2
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
Milll M	196	211	172	185	185	185
Mill N	171	125			124	124

Table 20 is models off-gas and specific NO_x 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_x concentrations, differences are to be examined.

Conjecture from reported values is done by changing some of the values by the thesis worker. Those values follow better the general trend.

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 same as in EIPPCB questionnaires. In table 22 some finnish mill locations names and the publically reported volumetric flue gas flows.

Table 22 BREF page 304 year 2007/2009

	Nm^3/ 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 of hardwood. Trend line can be drawn that the larger the off-gas flow, the more likely hardwood is used as raw material.

5.3 Typical wood consumption rate to produced pulp

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

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

	Mill B	**Mill C**	**Mill D**	**Mill E**
tons of pulp	618 700	603 524	585 187	509 962
total wood consumption 1000 m^3	3 406	3 061	3 211	2 336
wood per pulp m^3/t	5,5051	5,0719	5,4871	4,5807
pulp per wood t/m^3	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 C and reports higher off-gas volume (table 19). Mill E has higher hardwood rate than Mill C (table 18).

UPM reports in its annual report (2016) that typical average in mills is 4,44 m^3/ 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 higher yield than Nordic hardwood or softwood. UMP 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 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 even after changing to reference oxygen levels are higher or lower than excepted. In the model of combustion or through NO_x emission calculation made possible flows seen different than reported ones.

6.2 NO_x concentration to off-gas volumetric flow

If lower NOx concentration is due to larger volume of off-gas (in reference state), the environmental benefit of reducing NO_x concentration is not very beneficial. Figure 32 has some inclination. Every ball presents one mill.

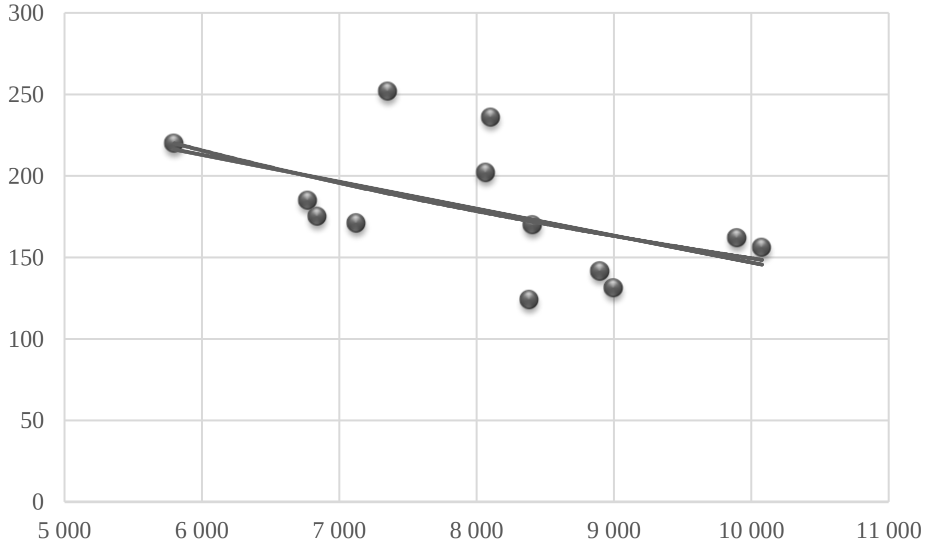


Figure 32 Reported flows and reported NOx concentration [mg/m^3n]. Trend line presents reported values NO_x concentration declines as volume grows [Nm^3/ADt]

Assumptions on, if Nordic hardwood produces higher NO_x concentration annual average than softwood is less correlating, but remarkable trend is to be found. Modelled concentrations and modelled flue gas-flow have lesser correlation.

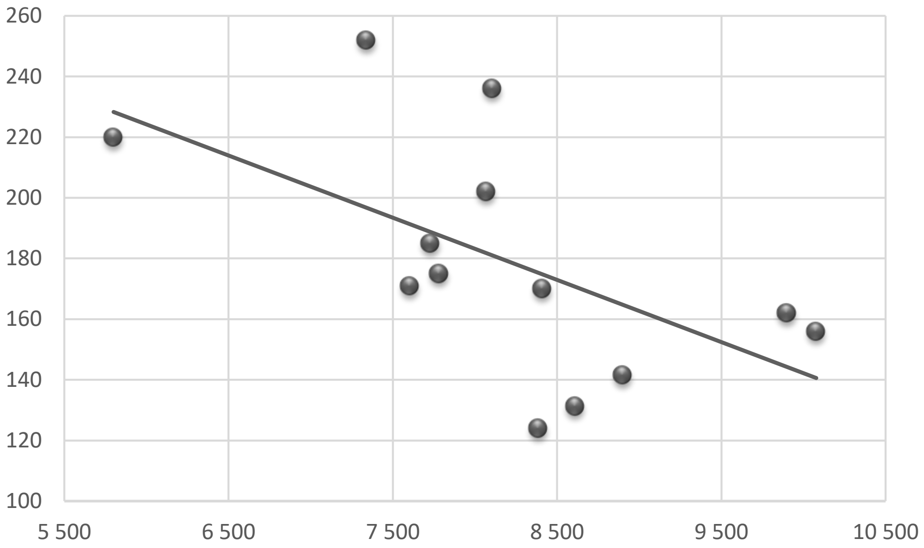


Figure 33 Conjecture flue gas to NOx concentration reported in EIPPC (2008).

Figure 33 presents thesis workers conjecture off-gas volume to reported NO_x concentration (mg/m^3n). As flue gases are more trend is that NO_x concentration level in it lowers. In figure 34 seemingly also for hardwood mills NO_x can be more.

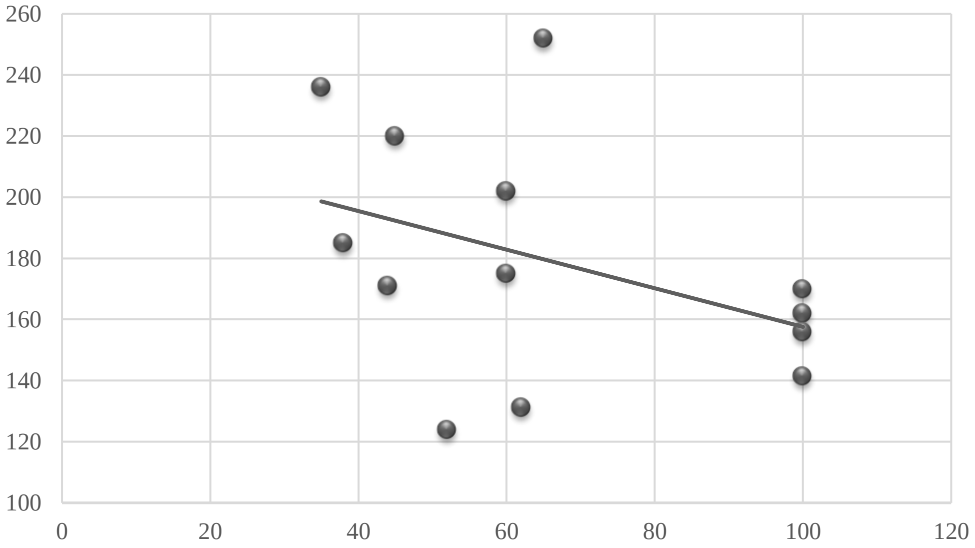


Figure 34 Reported NO_x and hardwood correlate less, but trend is down

Model of combustions and its NO_x concentration was created. In figure 35 shows resulting trend for modelled values for year 2016.

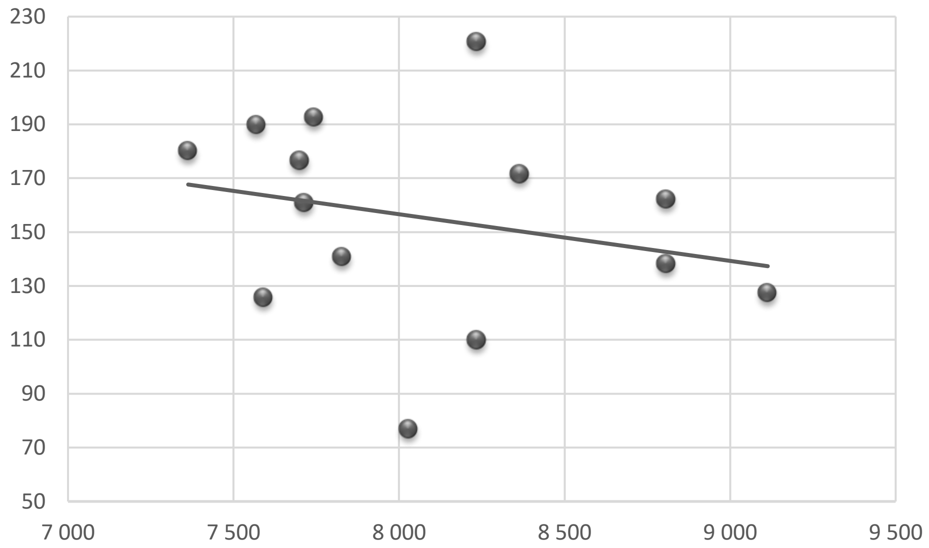


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Figure 35 Model of combustion and NO_x (mg/m^3n) 2016 to flue gas modelled.

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 year 2008, higher flue gas amount higher softwood usage.

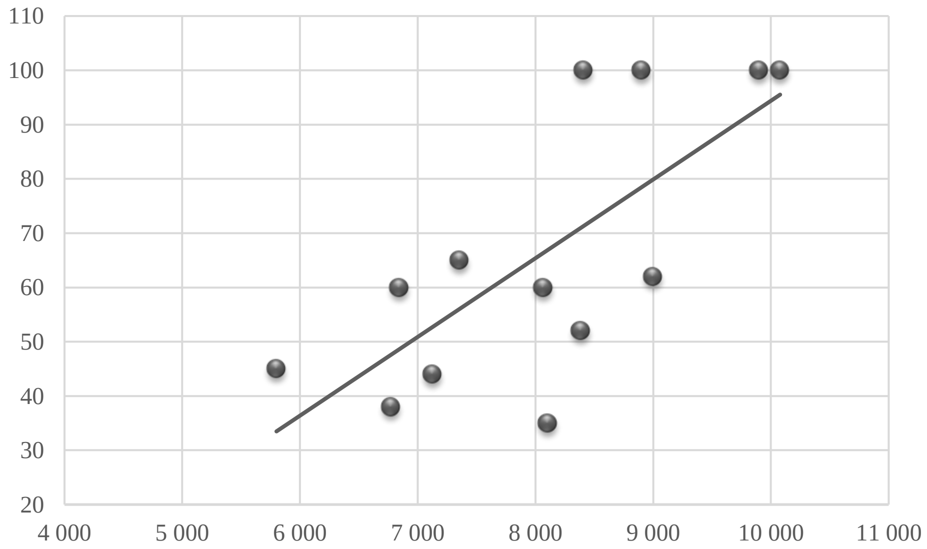

Figure 36 Reported flue gas flow to softwood-% reported along year 2008.

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

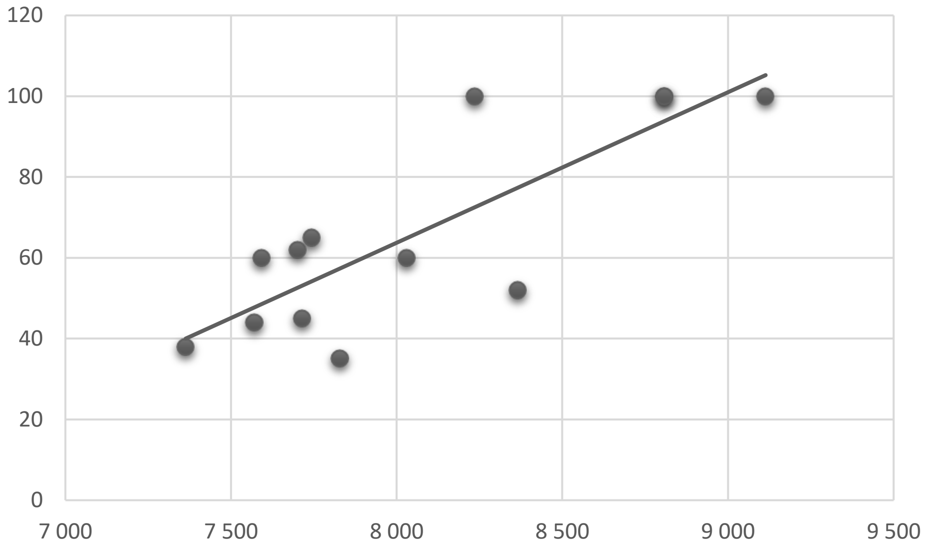

Figure 37 Model of combustion volume and reported softwood-%

Lastly conjecture, with small changes to reported flue gas flows is presented in figure 38. Here is exponential trend line.

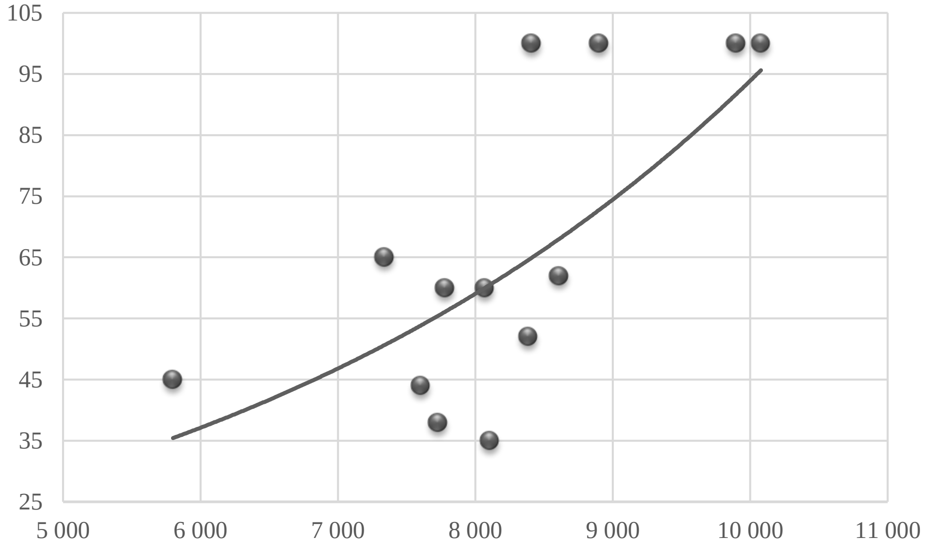

Figure 38 Conjecture Nm3/Adt and softwood content [%]

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. Future research could look for Nm3/ADt varying reasons numerically, if it is then that it effects to some parameters.

6.4 Specific emissions

Reported specific emissions for NO_x does not depend from flue gas amount seemingly, in figure 39.

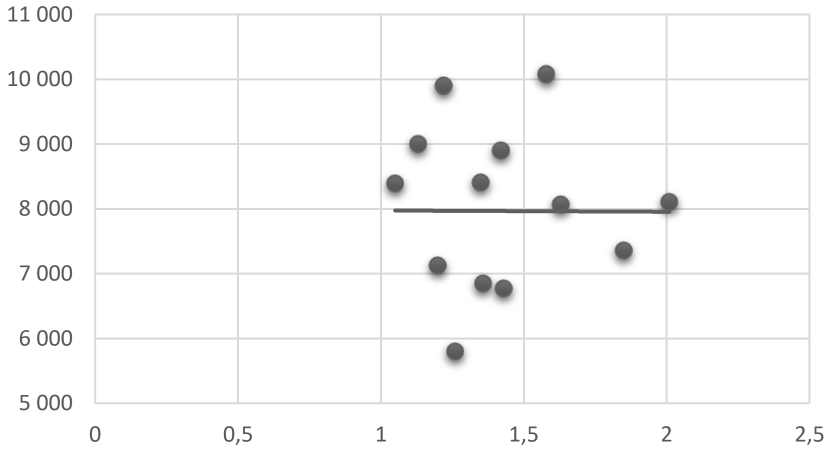

Figure 39 Reported volume Nm^3 to kg NO_x year 2008.

Both big and small volume of RB's flue gas produces higher or smaller specific emission of NO_x. Hardwood proportion in reported values show less dependency, in figure 40.

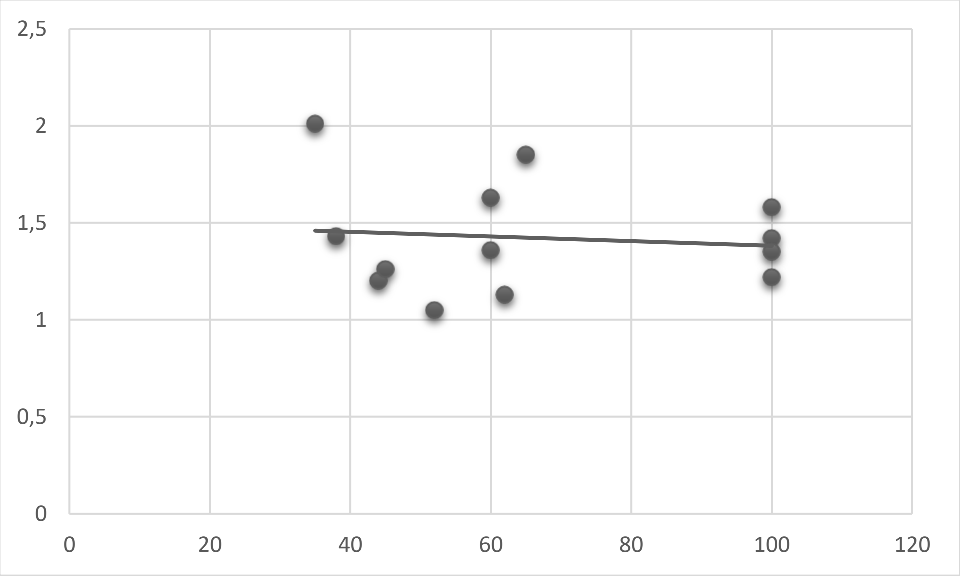

Figure 40 Reported kg/ADt and sw% year 2008.

Conjecture off-gas volume made by thesis worker from reported values and years 2016 approximated specific NO_x emissions present no sharp angle in trend line, in figure 41.

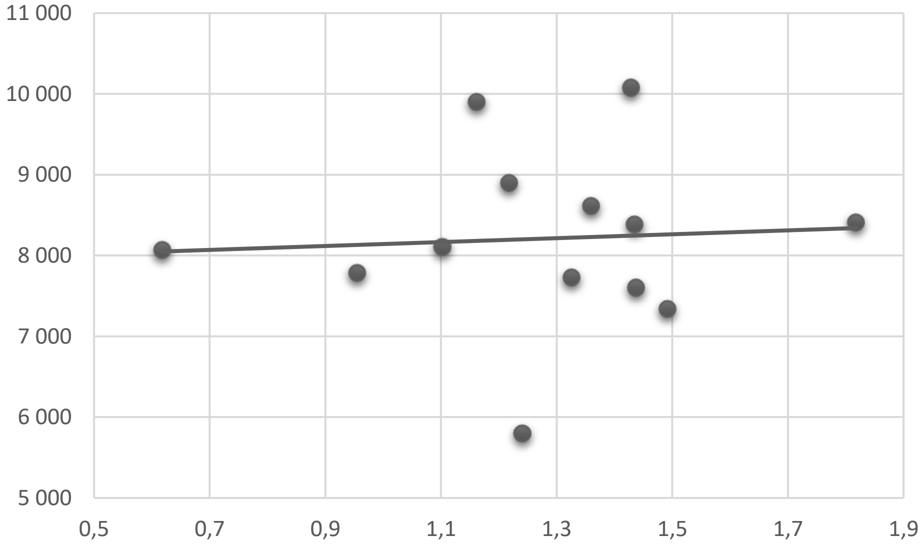

Figure 41 Conjecture volume and 2016 NO_x specif. emission in kg.

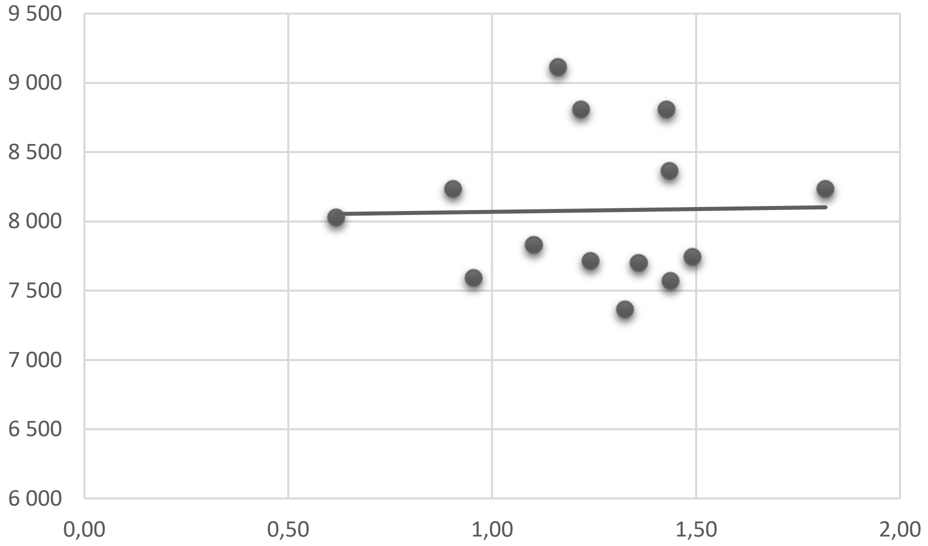

Figure 42 Year 2016 modelled flue gas volume Nm^3/ADt and recovery boiler NO$_x$ (kg/ADt) in year 2016.

Specific NO$_x$ per produced ton of pulp generate no changes from gas volumetric or hardwood consumption.

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. Mostly, for the balances to be plain, there must be implementing rule for giving the flue gas flows, same gas state. Also notification to water content and other certain parametric measurements in simultaneous time frame that are needed for qualified flue gas flow results.

Pulp mills have differences on their operation and flue gas amount that they produce to the surrounding atmosphere. Open policy on why some mills at least report lower exit gas flows indicating higher yield of pulp could help the overall industry to set better operation possibly.

The BREF PP 2015 table 8.4 in page 795 does not greatly differentiate between hardwood and softwood the concentration of NO_x. Due to higher yield and lower off-gas volume of hardwood most likely the concentration of NO_x tend to be higher than 200 mg/m^{3}n in some mills operating. Specific emission levels (kg NO_X/ADt) are more to be observed in recovery boiler for comparison. Generally some mills operate at too high dry solids content of black liquor and higher yield of pulp from wood, which is good for many reasons, but results higher NOx concentrations in off-gas.

One proportion is that if higher volume of flue gas per tonne of produced pulp – more material was released to the atmosphere and not utilized as bio-based product. Same atoms, where combusted to the air as has it was not been transmuted to useful chemical pulp or by-product. Energy recovery is the last utilizing method in pulp mill, but it remains the important for running the factory well.

Lignin has 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. Lignin markets still need to be established. Next steps in Finnish companies in coming years will be reducing 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 and several workers employ themselves in those places. 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 desirable product it is important to use different wood species in pulping. Species pine, spruce and birch are the main three by total mass in Nordic countries in kraft pulp mills. 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 results years 1990 – 2007 reduce in sulphuric air emissions, increasing 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 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 inside the mills environment and as well as emissions to air.

Reporting and measuring atmospheric emissions have in EU countries legal binding. Air emissions are averaged to annual period from the validated hourly data. Concentration and specific pollutant are reported. Periodic and continuous measurement are different. Relevant parameters for 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 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

BLACK LIQUOR	**units**
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
FW & STEAM	
FW	kg/s
CBD	kg/s
SB	kg/s
net steam	kg/s
AUX FUEL IN OPERATION	
load gas	m3n/s
start up gas	bar
load gas	bar
AIR	
primary left	m3n/s
primary right	m3n/s
secondary left	m3n/s
secondary right	m3n/s
load burner air	m3n/s
tertiary front	m3n/s
tertiary rear	m3n/s
Strong to combustion	m3n/s
Strong to combustion	kg/s
FLUE GAS	
CO left	ppm
CO right	ppm
SO2	mg/m3n
TRS	mg/m3n
NOx	mg/m3n
Dust	%
O2 after BB left	%, wet
O2 after BB right	%, wet

Hardwood model for the Mill G

Wood species in cooking	3		
Air dry unbleached cellulose	1745	t/24 h	355 days/y
Yield in Oxygen delignification	95	%	
Yield from wood to dry unbleached cellulose	54	%	48-55
Pulp kappa before oxygen delignification	18		
Pulp kappa after oxygen delignification	13		
Washing efficieny unbleached pulp	99	%	
Washing efficieny bleached pulp	99	%	
Soap recovery efficiency	80	%	
Water created when wood acids are neutralized	100	kg/t Bleached pulp	
NCG generation during cook	3	% wood	
Sulfur in NCG	2	kg/t Bleached pulp	
White liquor			
Active alkali, Na_2O-% per wood	19	%	
White liquor sufidity	40	%	
White liquor dry solids	15	%	
Causticity	80	%	
Reduction in white liquor	95	%	
Black liquor dry solids	73	%	
Oxidized White liquor			
Oxidized White liquor used in Oxygen deliginification	200	kg/t Bleached pulp	
Methanol formation in Oxygen deliginification	0,2	kg/t Bleached pulp	

Composition of formed black liquor dry solids

	Mill liquor			laboratory			laboratory	
C	33,9	%	C	33,84	%	Org acids	32,16	%
H	3,5	%	H	3,81	%	lignin	26,47	%
N	0,1	%				Soap	0,03	%
S	5,9	%	S	5,87	%	Other org	5,56	%
Na	19,3	%	Na	23,50	%	Org. Na	9,81	%
K	1,5	%				NaOH	4,83	%
Cl	0,3	%				Na_2S	12,92	%
O by diff	35,5	%	O	32,98	%	Na_2CO_3	5,70	%
Inorganics	26,9		SUM	67,02	%	Na_2SO_4	2,52	%
$S/(Na_2+K_2)$	41,76					SUM	100,00	%
Cl/(Na+K)	0,97							
K/(Na+K)	4,38							

Chemical composition of wood

		%
Cellulose	40	%
Hemicellulose	37	%
Lignin	20	%
Extractives	3	%
Summary	100	
Wood type	hardwood	

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**

				comparison
Organic compounds	Air dry bleached pulp pulp	1657,282	t/24h	2850
	Dry bleached pulp pulp	1492	t/24h	2565
	Dry unbleached cellulose	1570	t/24h	2700
	Dry wood needed	2908	t/24h	5870
	Wood needed to make 1000 kg unbleached	1852	kg/t Bleached pulp	2174
	Loss as volatiles (including TRS-compounds)	56	kg/t Bleached pulp	65
	TRS-compound loss (assumed as methylmerkaptan)	3	kg/t Bleached pulp	3
	Water generated when acids in wood are neutraloized	100	kg/t Bleached pulp	100
	Organic compounds in Black liquor	797	kg/t Bleached pulp	1110
	Organic compounds in pulp	996	kg/t Bleached pulp	995
	Lignin in wood to make 1 t of unbleached pulp	370	kg/t Bleached pulp	435
	Lignin in unbleached pulp	28	kg/t Bleached pulp	45
	Lignin in Black liquor	**342**	kg/t Bleached pulp	390
	Tall oil from rosins and fatty acids	2	kg/t Bleached pulp	2
	Tall oil remains	0	kg/t Bleached pulp	0
	Tall oil recovered	2	kg/t Bleached pulp	2
	Tall oil in black liquor	**0**	kg/t Bleached pulp	0
	Other organic compounds formation (4 % from wood)	74	kg/t Bleached pulp	87
	Other organic compounds to pulp	1	kg/t Bleached pulp	1
	Other organic compounds to Black liquor	**73**	kg/t Bleached pulp	86
	Organic acids to Black liquor	**381**	kg/t Bleached pulp	634
	Sum of Organic compounds to Black liquor	797	kg/t Bleached pulp	1110
	Lignin heating value	8597	kJ/kg Bleached pulp	9788
	Rosins and fatty acids heating value	15	kJ/kg Bleached pulp	15
	Organic acids heating value	5280	kJ/kg Bleached pulp	8597
	Other organic compounds heating value	1390	kJ/kg Bleached pulp	1632
	Sum of organic compounds heating value	15281	kJ/kg Bleached pulp	20031

White liquor	Active alkali, $NaOH$-% per dry wood	24	%	24
	Active alkali kg/t unbleached pulp, Na_2O	352	kg/t Bleached pulp	402
	Active alkali kg/t unbleached pulp, $NaOH$	449	kg/t Bleached pulp	514
	$NaOH$ charge as Na_2O	211	kg/t Bleached pulp	261
	$NaOH$ charge as $NaOH$	272	kg/t Bleached pulp	337
	Na_2S charge as Na_2O	141	kg/t Bleached pulp	141
	Na_2S charge as $NaOH$	182	kg/t Bleached pulp	182
	Active alkali concentration, Na_2O	115	g/l	112
	Active alkali concentration, $NaOH$	148	g/l	144
(estimate)	White liquor density	1169	g/l	1169
	Na_2CO_3 in white liquor as Na_2O	42	kg/t Bleached pulp	58
	Na_2SO_4 in white liquor as Na_2O	7	kg/t Bleached pulp	8
	Sum of inorganic compounds in white liquor	538	kg/t Bleached pulp	632
	Sum of inorganic compounds in white liquor as Na_2O	401	kg/t Bleached pulp	468
Black liquor	$NaOH$ in black liquor	50	kg/t Bleached pulp	114
	Organically bound Na in black liquor	129	kg/t Bleached pulp	129
	Na_2S in black liquor	170	kg/t Bleached pulp	170
	Na_2CO_3 in black liquor	71	kg/t Bleached pulp	97
	Na_2SO_4 in black liquor	16	kg/t Bleached pulp	19
	Inorganic compounds in black liquor	437	kg/t Bleached pulp	530
	Inorganic compounds, (Na_2S heating value)	2199	kJ/kg Bleached pulp	2199
Inorganic compounds in wood	$NaOH$ pulp	1	kg/t Bleached pulp	1
	Na in pulp organically bound	1	kg/t Bleached pulp	1
	Na_2S pulp	2	kg/t Bleached pulp	2
	Na_2CO_3 pulp	1	kg/t Bleached pulp	1
	Na_2SO_4 pulp	0	kg/t Bleached pulp	0
	Inorganic compounds pulp	4	kg/t Bleached pulp	5
	Black liquor dry solids from cooking	1234	kg/t Bleached pulp	1641
Oxygen stage	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
	Orgaanic acids to bleaching effluent	43	kg/t Bleached pulp	36
	Organic compounds in bleaching effluent	50	kg/t Bleached pulp	50

oxidized White liquor	White liquor oxidizing reaction: 2Na2S + 2O2 + H2O => Na2S2O3 + 2NaOH			
	Oxidized White liquor used in Oxygen deliginification	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 Na2S-content	33	%	28
	Unoxidized White liquorNaOH-content	51	%	53
	Unoxidized White liquor Na2CO3-content	13	%	16
	Unoxidized White liquor Na2SO4-content	3	%	3
	TOTAL	100	%	100
	White liquor oxidiation reaction: 2Na2S + 2O2 + H2O => Na2S2O3 + 2NaOH			
	Na2S in one ton of unoxidized White liquor	49	kg/t WL unoxidated	42
	$Na_2S_2O_3$ 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
	Na2S2O3 in oxidized White liquor	50	kg/1021 kg WL oxidated	43
	Na2CO3 in oxidized White liquor	20	kg/1021 kg WL oxidated	23
	Na2SO4 in oxidized White liquor	4	kg/1021 kg WL oxidated	5
	Water in oxidized White liquor	844	kg/1021 kg WL oxidated	845
	Sum of oxidized White liquor	1020	kg	1017
	Oxygen deliginification Na2S2O3 oxidized fully to Na2SO4			
	$Na_2S_2O_3 + 2O_2 + 2NaOH \Rightarrow 2Na_2SO_4 + H_2O$			
	Oxygen deliginification NaOH used to oxidize thiosulfate	25	kg/1021 kg WL oxidated	21,55
	Oxygen deliginification Na2SO4 created in oxidizing thiosulfate	90	kg/1021 kg WL oxidated	76,49
	Oxygen deliginification H2O created in oxidizing thiosulfate	6	kg/1021 kg WL oxidated	4,85
	Sum of water and inorganics in Bleaching residue	1091	kg	1077
	NaOH in oxygen bleaching residue	14	kg/t Bleached pulp	15
	Na2S2O3 in oxygen bleaching residue	0	kg/t Bleached pulp	0
	Na2CO3 in oxygen bleaching residue	4	kg/t Bleached pulp	4
	Na2SO4 in oxygen bleaching residue	17	kg/t Bleached pulp	15
	Sum of Inorganic compounds to bleaching effluent	35	kg/t Bleached pulp	34
	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
	Na2S2O3 heating value in in Bleaching residue	0	kJ/kg Bleached pulp	0
	Bleaching residue heating value yhteensä	765	kJ/kg Bleached pulp	839
	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-%, d	33,95	33,9
H	mass-%, d	3,53	3,4
N	mass-%, d	0,10	0,1
S	mass-%, d	5,87	5,9
Na	mass-%, d	19,26	19,3
K	mass-%, d	1,50	1,5
Cl	mass-%, d	0,30	0,3
Inorganics	mass-%, d	26,9	26,9
Dry solids	%	73	73
Air ratio	-	1,164	1,164

									NetHeat	kW/kgds	7973	8037	
									Air at 1.0	m3n/kgds	2,93	2,89	
	Black liquor total heating value			**18246**	kJ/kg Bleached pulp	23070			Air at 1.x	m3n/kgds	3,410	3,363	
									Air/HHV	m3n/MJ	0,212	0,209	
	Black liquor Dry solids heating value			**13834**	kJ/kg BLDS	13375			FG at 1.x	m3n/kgds	4,269	4,220	
									FG/HHV	m3n/MJ	0,309	0,305	
	Dry solids to recovery boiler			1319	kg/t Bleached pulp	1725			FGdry at 1	m3n/kgds	3,664	3,625	
	Dry solids organic matter content			64,22	%	67							
	Black liquor to recovery boiler			1807	kg/t Bleached pulp	2464			Fg	m3n/s	**113,68**		5630 m3n(wet)/A
(estimate)	Black liquor density			1400	g/l	1400				kg/s	140,3		
									Air	m3n/s	78,0		
	Flue gases						Fg from hw	Fg form sw		kg/s	100,0		
				4832	m3n/Adt	5798	3189,016	3470,202	FG(dry)	m3n/s	**97,56**		4831,84 m3n(dry)/A
							6659,218	combined		kg/s	120,4		
	Heat to recovery boiler			**18,25**	GJ/t Bleached pulp	23,07				5630,389	m3n(wet)/Adt		
		"		**0,332**	GJ/s	0,721							
		Moolmass											
	Na_2O	61,97894	g/mol							4831,842	m3n(dry)/Adt		
	NaOH	39,99707	"										
	Alkali conversion NaOH		=	1,290666475	Na_2O								

									NetHeat	kW/kgds	7973	8037	
									Air at 1.0	m3n/kgds	2,93	2,89	
	Black liquor total heating value			**18246**	kJ/kg Bleached pulp	23070			Air at 1.x	m3n/kgds	3,410	3,363	
									Air/HHV	m3n/MJ	0,212	0,209	
	Black liquor Dry solids heating value			**13834**	kJ/kg BLDS	13375			FG at 1.x	m3n/kgds	4,269	4,220	
									FG/HHV	m3n/MJ	0,309	0,305	
	Dry solids to recovery boiler			1319	kg/t Bleached pulp	1725			FGdry at 1	m3n/kgds	3,664	3,625	
	Dry solids organic matter content			64,22	%	67							
	Black liquor to recovery boiler			1807	kg/t Bleached pulp	2464			Fg	m3n/s	**113,68**		5630 m3n(wet)/A
(estimate)	Black liquor density			1400	g/l	1400				kg/s	140,3		
									Air	m3n/s	78,0		
	Flue gases						Fg from hw	Fg form sw		kg/s	100,0		
				4832	m3n/Adt	5798	3189,016	3470,202	FG(dry)	m3n/s	**97,56**		4831,84 m3n(dry)/A
							6659,218	combined		kg/s	120,4		
	Heat to recovery boiler			**18,25**	GJ/t Bleached pulp	23,07				5630,389	m3n(wet)/Adt		
		"		**0,332**	GJ/s	0,721							
		Moolmass											
	Na_2O	61,97894	g/mol							4831,842	m3n(dry)/Adt		
	NaOH	39,99707	"										
	Alkali conversion NaOH		=	1,290666475	Na_2O								

Wood species

Pine
Spruce
Birch
Euca
Other

Compounds in liquor and their heating values

		SI heating value				C %	H %	O %	Na %	S %	Muut %	yht
	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				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
J. Gullichsenin corresponding values are:		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											
	$Na_2S_2O_3$	5790	kJ/kg			0	0	30	29	41	0	100
	Na_2S	12900	kJ/kg			0	0	0	59	41	0	100
	Na_2SO_4	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_2CO_3	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_3SH	26100	kJ/kg
CH_3SCH_3	30900	kJ/kg
CH_3SSCH_3	23600	kJ/kg
methanol	22300	kJ/kg
turpentine	29200	kJ/kg
REACTION HEATS	465	MJ/t pulp

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
		softwood	softwood	hardwood	hardwood	
Summary		100	100	100	100	0

Softwood model for the Mill G

Wood species in cooking	1		
Air dry unbleached cellulose	1427	t/24 h	355 days/y
Yield in Oxygen delignification	96	%	
Yield from wood to dry unbleached cellulose	48	%	40-48
Pulp kappa before oxygen delignification	28		
Pulp kappa after oxygen delignification	14		
Washing efficieny unbleached pulp	99	%	
Washing efficieny bleached pulp	99	%	
Soap recovery efficiency	80	%	
Water created when wood acids are neutralized	100	kg/t Bleached pulp	
NCG generation during cook	3	% wood	
Sulfur in NCG	2	kg/t Bleached pulp	
White liquor			
Active alkali, Na_2O-% per wood	18,6	%	
White liquor sufidity	40	%	
White liquor dry solids	15	%	
Causticity	82	%	
Reduction in white liquor	94	%	
Black liquor dry solids	73	%	
Oxidized White liquor			
Oxidized White liquor used in Oxygen deliginification	200	kg/t Bleached pulp	
Methanol formation in Oxygen deliginification	0,2	kg/t Bleached pulp	

Composition of formed black liquor dry solids

	Mill liquor			laboratory			laboratory	
C	36,7	%	C	38,23	%	Org acids	27,48	%
H	3,8	%	H	4,01	%	lignin	34,09	%
N	0,1	%				Soap	0,29	%
S	5,4	%	S	5,42	%	Other org	5,21	%
Na	17,5	%	Na	21,31	%	Org. Na	8,17	%
K	1,5	%				NaOH	5,75	%
Cl	0,3	%				Na_2S	11,89	%
O by diff	34,7	%	O	31,02	%	Na_2CO_3	4,69	%
Inorganics	24,7		SUM	68,98	%	Na_2SO_4	2,44	%
S/(Na2+K2)	42,31					SUM	100,00	%
Cl/(Na+K)	1,06							
K/(Na+K)	4,80							

Chemical composition of wood

		%
Cellulose	39	%
Hemicellulose	30	%
Lignin	27	%
Extractives	4	%
Summary	100	
Wood type	softwood	

Heating value of black liquor dry-solids	**15061**	**kJ/kg BLDS**
Heat in to recovery boiler	**23,849**	**GJ/t Bleached pulp**
Heat in to recovery boiler per second	**0,355**	**GJ/s**
Massflow to recovery boiler	**2153,5**	**tDS/24h**
Massflow to recovery boiler	**24,9**	**kgDS/s**

Organic compoun	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 neutraloized	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	**520**	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	**5**	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	**83**	kg/t Bleached pulp	86
Organic acids to Black liquor	**415**	kg/t Bleached pulp	634
Sum of Organic compounds to Black liquor	1022	kg/t Bleached pulp	1110

Lignin heating value	13167	kJ/kg Bleached pulp	9788	Heating val	kJ/BDt	14148
Rosins and fatty acids heating value	170	kJ/kg Bleached pulp	15	Heating val	kJ/BDt	174
Organic acids heating value	5746	kJ/kg Bleached pulp	8597	Heating val	kJ/BDt	7393
Other organic compounds heating value	1564	kJ/kg Bleached pulp	1632	Heating val	kJ/BDt	1254
Sum of organic compounds heating value	20648	kJ/kg Bleached pulp	20031	Heating val	kJ/BDt	0
				Heating v	kJ/BDt	22968

White liquor	Active alkali, NaOH-% per dry wood	24	%	24
	Active alkali kg/t unbleached pulp, Na2O	388	kg/t Bleached pulp	402
	Active alkali kg/t unbleached pulp, NaOH	495	kg/t Bleached pulp	514
	NaOH charge as Na2O	233	kg/t Bleached pulp	261
	NaOH charge as NaOH	300	kg/t Bleached pulp	337
	Na2S charge as Na2O	155	kg/t Bleached pulp	141
	Na2S charge as NaOH	200	kg/t Bleached pulp	182

	Active alkali concentration, Na_2O	116	g/l	112
	Active alkali concentration, $NaOH$	149	g/l	144
(estimate)	White liquor density	1169	g/l	1169
	Na_2CO_3 in white liquor as Na_2O	42	kg/t Bleached pulp	58
	Na_2SO_4 in white liquor as Na_2O	9	kg/t Bleached pulp	8
	Sum of inorganic compounds in white liquor	588	kg/t Bleached pulp	632
	Sum of inorganic compounds in white liquor as Na_2O	439	kg/t Bleached pulp	468
Black liquor	$NaOH$ in black liquor	77	kg/t Bleached pulp	114
	Organically bound Na in black liquor	129	kg/t Bleached pulp	129
	Na_2S in black liquor	188	kg/t Bleached pulp	170
	Na_2CO_3 in black liquor	71	kg/t Bleached pulp	97
	Na_2SO_4 in black liquor	21	kg/t Bleached pulp	19
	Inorganic compounds in black liquor	487	kg/t Bleached pulp	530
	Inorganic compounds, (Na_2S heating value)	2428	kJ/kg Bleached pulp	2199
Inorganic compounds in wood	$NaOH$ pulp	1	kg/t Bleached pulp	1
	Na in pulp organically bound	1	kg/t Bleached pulp	1
	Na_2S pulp	2	kg/t Bleached pulp	2
	Na_2CO_3 pulp	1	kg/t Bleached pulp	1
	Na_2SO_4 pulp	0	kg/t Bleached pulp	0
	Inorganic compounds pulp	5	kg/t Bleached pulp	5
	Black liquor dry solids from cooking	1509	kg/t Bleached pulp	1641
Oxygen stage	Bleached pulp formation	960	kg/t Bleached pulp	950
	Bleached pulp inorganic compounds	5	kg/t Bleached pulp	6
	Bleached pulp organic compounds	955	kg/t Bleached pulp	944
	Loss of unbleached pulp during bleaching	40	kg/t Bleached pulp	50
	Lignin in bleached pulp	23	kg/t Bleached pulp	31
	Lignin dissolved to bleaching effluent	19	kg/t Bleached pulp	14

	Metanol creation	0,2	kg/t Bleached pulp	0
	Orgaanic acids to bleaching effluent	20	kg/t Bleached pulp	36
	Organic compounds in bleaching effluent	40	kg/t Bleached pulp	50
oxidized White liquor	White liquor oxidizing reaction: 2Na2S + 2O2 + H2O => Na2S2O3 + 2NaOH			
	Oxidized White liquor used in Oxygen deliginification	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 Na2S-content	33	%	28
	Unoxidized White liquorNaOH-content	51	%	53
	Unoxidized White liquor Na2CO3-content	12	%	16
	Unoxidized White liquor Na2SO4-content	4	%	3
	TOTAL	100	%	100

White liquor oxidiation reaction: 2Na2S + 2O2 + H2O => Na2S2O3 + 2NaOH

Na_2S in one ton of unoxidized White liquor	50	kg/t WL unoxidated	42
$Na_2S_2O_3$ 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
$Na_2S_2O_3$ in oxidized White liquor	50	kg/1021 kg WL oxidat	43
Na_2CO_3 in oxidized White liquor	18	kg/1021 kg WL oxidat	23
Na_2SO_4 in oxidized White liquor	5	kg/1021 kg WL oxidat	5
Water in oxidized White liquor	844	kg/1021 kg WL oxidat	845
Sum of oxidized White liquor	1020	kg	1017

Oxygen deliginification $Na_2S_2O_3$ oxidized fully to Na_2SO_4

$Na_2S_2O_3 + 2O_2 + 2NaOH \Rightarrow 2Na_2SO_4 + H_2O$

Oxygen deliginification NaOH used to oxidize thiosulfate	26	kg/1021 kg WL oxidat	21,55
Oxygen deliginification Na_2SO_4 created in oxidizing thiosulfate	91	kg/1021 kg WL oxidat	76,49
Oxygen deliginification H_2O created in oxidizing thiosulfate	6	kg/1021 kg WL oxidat	4,85
Sum of water and inorganics in Bleaching residue	1091	kg	1077

	$NaOH$ in oxygen bleaching residue	14	kg/t Bleached pulp	15
	$Na_2S_2O_3$ in oxygen bleaching residue	0	kg/t Bleached pulp	0
	Na_2CO_3 in oxygen bleaching residue	3	kg/t Bleached pulp	4
	Na_2SO_4 in oxygen bleaching residue	18	kg/t Bleached pulp	15
	Sum of Inorganic compounds to bleaching effluent	35	kg/t Bleached pulp	34
	Dry solids in Bleaching residue	**75**	kg/t Bleached pulp	84
Bleaching residue heating value	Lignin heating value in Bleaching residue	492	kJ/kg Bleached pulp	357
	Organic acids heating value in Bleaching residue	282	kJ/kg Bleached pulp	482
	$Na_2S_2O_3$ heating value in in Bleaching residue	0	kJ/kg Bleached pulp	0
	Bleaching residue heating value yhteensä	774	kJ/kg Bleached pulp	839
	Sum of Black liquor and Bleaching residue Dry solids	1584	kg/t Bleached pulp	1725
	Black liquor total heating value	**23849**	kJ/kg Bleached pulp	23070
	Black liquor Dry solids heating value	**15061**	kJ/kg BLDS	13375
	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
(estimate)	Black liquor density	1400	g/l	1400
	Flue gases			
		6426	m3n(dry)/Adt	7712
	Heat to recovery boiler	**23,85**	GJ/t Bleached pulp	23,07
	"	**0,355**	GJ/s	0,721

	Moolmass	
Na_2O	61,97894	g/mol
$NaOH$	39,99707	"

Alkali conversion NaOH = 1,290666475 Na_2O

Liquor analysis		Design value	Estimate from HHV
Flow	Tds/d	2260,2	
HHV	MJ/kgds	15,06	15,1
C	mass-%, d	36,65	36,7
H	mass-%, d	3,81	3,7
N	mass-%, d	0,10	0,1
S	mass-%, d	5,42	5,4
Na	mass-%, d	17,50	17,5
K	mass-%, d	1,50	1,5
Cl	mass-%, d	0,30	0,3
Inorganics	mass-%, d	24,7	24,7
Dry solids	%	73	73
Air ratio	-	1,164	1,164
NetHeat	kW/kgds	9245	9313
Air at 1.0	m3n/kgds	3,26	3,21
Air at 1.x	m3n/kgds	3,790	3,739
Air/HHV	m3n/MJ	0,216	0,213
FG at 1.x	m3n/kgds	4,690	4,637
FG/HHV	m3n/MJ	0,311	0,308
FGdry at 1	m3n/kgds	4,058	4,017

Fg(wet)	m3n/s	**122,68**	7426
	kg/s	151,4	
Air	m3n/s	85,2	
	kg/s	109,2	
FG(dry)	m3n/s	**106,16**	6426,30
	kg/s	131,0	

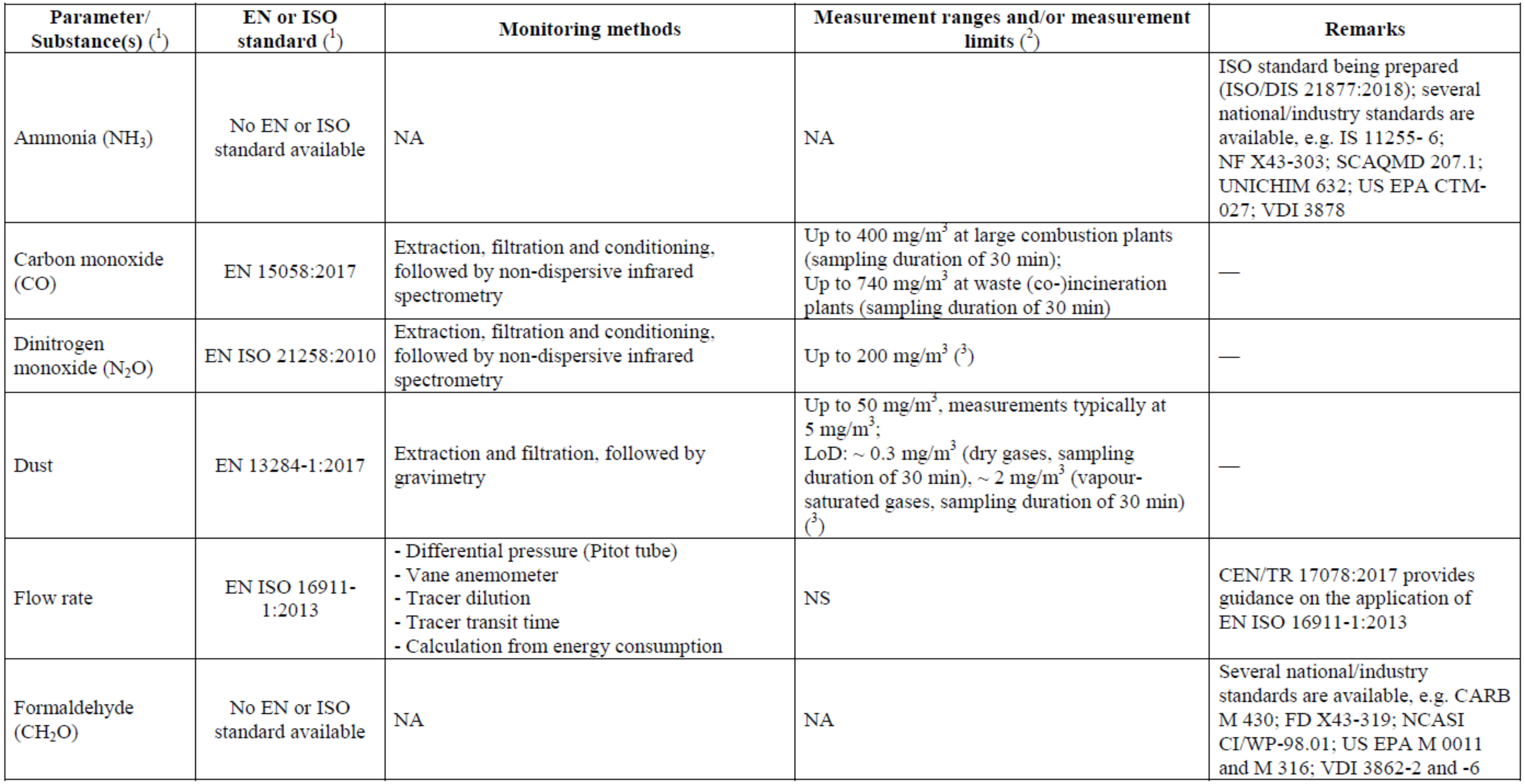
Wood species Compounds in liquor and their heating values

Pine		SI heating value				C %	H %	O %	Na %	S %	Muut %	yht
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			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
J. Gullichsen:		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											
	$Na_2S_2O_3$	5790	kJ/kg			0	0	30	29	41	0	100
	Na_2S	12900	kJ/kg			0	0	0	59	41	0	100
	Na_2SO_4	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_2CO_3	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_3SH	26100	kJ/kg									
	CH_3SCH_3	30900	kJ/kg									
	CH_3SSCH_3	23600	kJ/kg									
	methanol	22300	kJ/kg									
	turpentine	29200	kJ/kg									
	REACTION HEATS	465	MJ/t pulp									

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
		softwood	softwood	hardwood	hardwood	
Summary		100	100	100	100	0

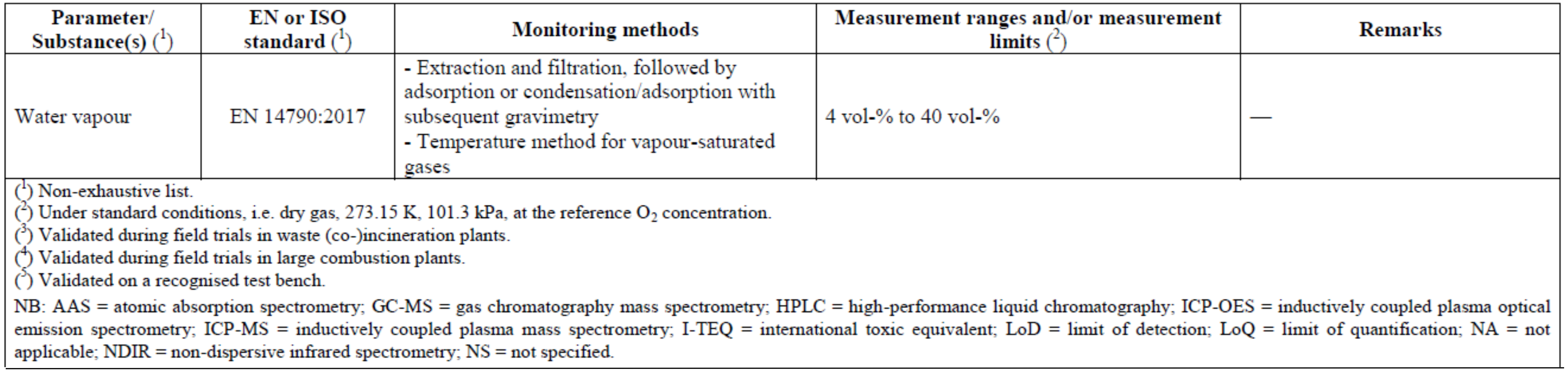
Periodic measurement of emissions to air EU specific standards (Brinkmann et al. 2018, 127 – 130)



Parameter/ Substance(s) (1)	EN or ISO standard (1)	Monitoring methods	Measurement ranges and/or measurement limits (2)	Remarks
Ammonia (NH_3)	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^3 at large combustion plants (sampling duration of 30 min); Up to 740 mg/m^3 at waste (co-)incineration plants (sampling duration of 30 min)	—
Dinitrogen monoxide (N_2O)	EN ISO 21258:2010	Extraction, filtration and conditioning, followed by non-dispersive infrared spectrometry	Up to 200 mg/m^3 (3)	—
Dust	EN 13284-1:2017	Extraction and filtration, followed by gravimetry	Up to 50 mg/m^3, measurements typically at 5 mg/m^3; LoD: ~ 0.3 mg/m^3 (dry gases, sampling duration of 30 min), ~ 2 mg/m^3 (vapour-saturated gases, sampling duration of 30 min) (3)	—
Flow rate	EN ISO 16911-1:2013	- Differential pressure (Pitot tube) - Vane anemometer - Tracer dilution - Tracer transit time - Calculation from energy consumption	NS	CEN/TR 17078:2017 provides guidance on the application of EN ISO 16911-1:2013
Formaldehyde (CH_2O)	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) (1)	EN or ISO standard (1)	Monitoring methods	Measurement ranges and/or measurement limits (2)	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^3 to 5 000 mg/m^3 (3); LoD: ~ 0.2 mg/m^3 (sample gas volume of 0.4 m^3 to 0.5 m^3, 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^3; LoD: ~ 0.1 mg/m^3 (sample gas volume of 0.1 m^3)	—
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 $KMnO_4/H_2SO_4$ or $K_2Cr_2O_7/HNO_3$); subsequent digestion of the filter; final analysis of the aqueous samples by AAS	1 µg/m^3 to 500 µg/m^3 (3); LoD: 2.6 µg/m^3 (sample gas volume of 0.05 m^3)	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_2O_2/HNO_3); subsequent digestion of the filter; final analysis of the aqueous samples by AAS, ICP-OES or ICP-MS	5 µg/m^3 to 500 µg/m^3 (for each element) (3); Required LoD: ≤ 1 µg/m^3 for each element and sampling train; Resulting LoD: 5 µg/m^3 for the whole sampling train	—
Methane (CH_4)	EN ISO 25139:2011	Extraction, filtration and conditioning, followed by gas chromatography with flame ionisation detection	Up to 1 500 mg/m^3	—
Nitrogen oxides (NO_X)	EN 14792:2017	Extraction, filtration and conditioning, followed by chemiluminescence (after conversion to NO and reaction with ozone)	Up to 1 300 mg/m^3 at large combustion plants; Up to 400 mg/m^3 at waste (co-)incineration plants	—
Odour	EN 13725:2003	Dynamic olfactometry	Measurements typically from 10^1 ou_E/m^3 to 10^7 ou_E/m^3 (including predilution); Detection threshold: 1 ou_E/m^3	AC:2006 (Technical corrigendum)
Oxygen (O_2)	EN 14789:2017	Extraction, filtration and conditioning, followed by paramagnetism	3 vol-% to 21 vol-% (sampling duration of 30 min) (3) (4) (5)	—
$PM_{10}/PM_{2.5}$	EN ISO 23210:2009	Impactors, followed by gravimetry	LoD: PM_{10}: 0.4 mg/m^3 (sample gas volume: 1 m^3, sampling duration of ~ 30 min) LoD: $PM_{2.5}$: 0.3 mg/m^3 (sample gas volume: 1 m^3, sampling duration of ~ 30 min)	—

Parameter/ Substance(s) (1)	EN or ISO standard (1)	Monitoring methods	Measurement ranges and/or measurement limits (2)	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^3 to 0.57 pg WHO-TEQ/m^3, LoQ: 0.20 pg WHO-TEQ/m^3 to 1.37 pg WHO-TEQ/m^3 (depending on sampling method) (3)	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^3; LoQ: 0.1 pg/m^3 to 8.8 pg/m^3 for individual congeners (3) (corresponds to a LoQ of 1.2 pg I-TEQ/m^3 to 3.7 pg I-TEQ/m^3)	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^3 to 1 μg/m^3 for 6 m^3 sample volume and a dilution factor of 100	—
Sulphur oxides (SO_X)	EN 14791:2017	Extraction and filtration, followed by absorption in aqueous H_2O_2 solution with subsequent sulphate determination via a) ion chromatography or b) titration	a) Ion chromatography: 0.5 mg/m^3 to 2 000 mg/m^3 (sampling duration of 30 min) (3) (4); LoQ: ≥ 0.1 mg/m^3 (flow rate of 1 l/min, 100 ml of absorption solution, sampling duration of 30 min) b) Titration: 5 mg/m^3 to 2 000 mg/m^3 (sampling duration of 30 min) (3) (4); LoQ ≥ 2.2 mg/m^3 (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^3	—
	EN ISO 13199:2012	Extraction and filtration, followed by catalytic conversion and NDIR	From about 70 mg/m^3 to 600 mg/m^3	Not applicable to combustion processes



Parameter/ Substance(s) (1)	**EN or ISO standard** (1)	**Monitoring methods**	**Measurement ranges and/or measurement limits** (2)	**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-%	—

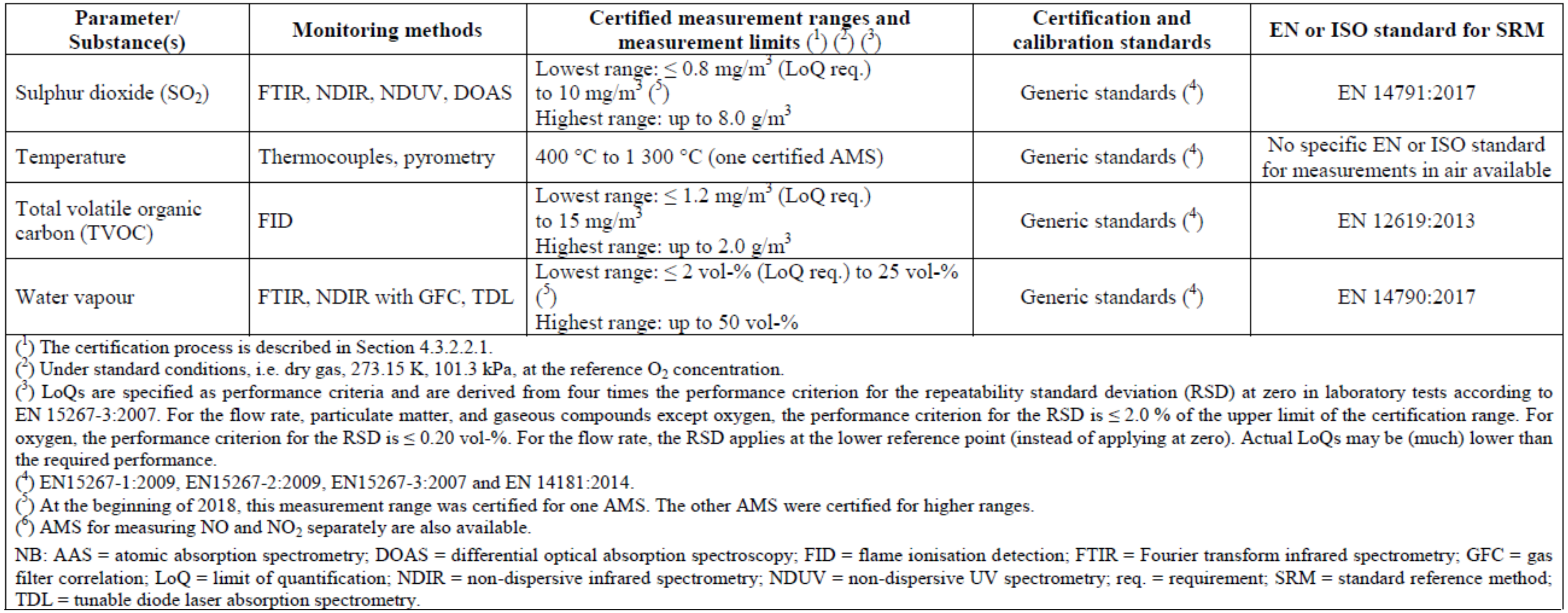
(1) Non-exhaustive list.
(2) Under standard conditions, i.e. dry gas, 273.15 K, 101.3 kPa, at the reference O_2 concentration.
(3) Validated during field trials in waste (co-)incineration plants.
(4) Validated during field trials in large combustion plants.
(5) Validated on a recognised test bench.

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.

*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 (1) (2) (3)	Certification and calibration standards	EN or ISO standard for SRM
Ammonia (NH_3)	FTIR, NDIR with GFC, TDL	Lowest range: ≤ 0.4 mg/m^3 (LoQ req.) to 5 mg/m^3 (5) Highest range: up to 500 mg/m^3	Generic standards (4)	No EN or ISO standard available
Carbon monoxide (CO)	FTIR, NDIR	Lowest range: ≤ 4 mg/m^3 (LoQ req.) to 50 mg/m^3 Highest range: up to 10 g/m^3	Generic standards (4)	EN 15058:2017
Dinitrogen monoxide (N_2O)	FTIR, NDIR	Lowest range: ≤ 1.6 mg/m^3 (LoQ req.) to 20 mg/m^3 Highest range: up to 9.8 g/m^3 (given as 5 000 ppm)	Generic standards (4)	EN ISO 21258:2010
Dust	Light attenuation or scattering, triboelectric	Lowest range: ≤ 0.12 mg/m^3 (LoQ req.) to 1.5 mg/m^3 (given as 5 scattered light units) (5) Highest range: up to 300 mg/m^3 (given as 20 000 scattered light units)	Generic standards (4) 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 (4) 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^3 (LoQ req.) to 10 mg/m^3 (5) Highest range: up to 5.0 g/m^3	Generic standards (4)	EN 1911:2010
Hydrogen fluoride (HF)	FTIR, TDL	Lowest range: ≤ 0.08 mg/m^3 (LoQ req.) to 1 mg/m^3 (5) Highest range: up to 300 mg/m^3	Generic standards (4)	ISO 15713:2006
Methane (CH_4)	FID, FTIR, NDIR	Lowest range: ≤ 0.6 mg/m^3 (LoQ req.) to 7.5 mg/m^3 (5) Highest range: up to 500 mg/m^3	Generic standards (4) and EN ISO 25140:2010	EN ISO 25139:2011
Mercury (Hg)	AAS, DOAS	Lowest range: ≤ 0.4 µg/m^3 (LoQ req.) to 5 µg/m^3 (5) Highest range: up to 1 mg/m^3	Generic standards (4) and EN 14884:2005	EN 13211:2001
Nitrogen oxides (NO_X) (6)	Chemiluminescence, FTIR, NDIR, NDUV, DOAS	Lowest range: ≤ 1.6 mg/m^3 (LoQ req.) to 20 mg/m^3 (5) Highest range: up to 7.5 g/m^3	Generic standards (4)	EN 14792:2017
Oxygen (O_2)	Paramagnetism, electrochemical cell, zirconia (ZrO_2)	Lowest range: ≤ 0.8 vol-% (LoQ req.) to 5 vol-% Highest range: up to 25 vol-%	Generic standards (4)	EN 14789:2017



Parameter/ Substance(s)	**Monitoring methods**	**Certified measurement ranges and measurement limits** (1) (2) (3)	**Certification and calibration standards**	**EN or ISO standard for SRM**
Sulphur dioxide (SO_2)	FTIR, NDIR, NDUV, DOAS	Lowest range: ≤ 0.8 mg/m^3 (LoQ req.) to 10 mg/m^3 (5) Highest range: up to 8.0 g/m^3	Generic standards (4)	EN 14791:2017
Temperature	Thermocouples, pyrometry	400 °C to 1 300 °C (one certified AMS)	Generic standards (4)	No specific EN or ISO standard for measurements in air available
Total volatile organic carbon (TVOC)	FID	Lowest range: ≤ 1.2 mg/m^3 (LoQ req.) to 15 mg/m^3 Highest range: up to 2.0 g/m^3	Generic standards (4)	EN 12619:2013
Water vapour	FTIR, NDIR with GFC, TDL	Lowest range: ≤ 2 vol-% (LoQ req.) to 25 vol-% (5) Highest range: up to 50 vol-%	Generic standards (4)	EN 14790:2017

(1) The certification process is described in Section 4.3.2.2.1.

(2) Under standard conditions, i.e. dry gas, 273.15 K, 101.3 kPa, at the reference O_2 concentration.

(3) 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.

(4) EN15267-1:2009, EN15267-2:2009, EN15267-3:2007 and EN 14181:2014.

(5) At the beginning of 2018, this measurement range was certified for one AMS. The other AMS were certified for higher ranges.

(6) AMS for measuring NO and NO_2 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.