KARELIA UNIVERSITY OF APPLIED SCIENCES
Sustainable energy economy
Master's Thesis

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PRODUCTION OF RENEWABLE CO_2 NEUTRAL ENERGY AS A BYPRODUCT FROM KRAFT BLACK LIQUOR IN RECOVERY BOILERS

Recovery Boilers of new generation with Improved Energy Production

Thesis
August 2021

THESIS
August 2021
Master Degree Programme in
Energy and Environmental Technology

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Title
Production of Renewable CO_2 Neutral Energy As a Byproduct From Kraft Black Liquor In Recovery Boilers- Recovery Boilers of New Generation With Improved Energy Production

Commissioned by Andritz Oy

Abstract

Recovery boiler plays an essential role in the production of pulp and paper products. In recent years, pulp and paper industry has undergone significant changes and the renewal process is going on intensively. Recovery boilers of new generation with high-energy production and fewer emissions ensure universal access to affordable, reliable, and modern energy services.

The main target of the study is to review possible boilers' technologies to produce clean energy and to compare its power-to-emission ratio with other kinds of boilers. The thesis is directed to prove the advantages of recovery boilers with improved energy production (RBIEP) to generate CO_2 neutral energy.

The calculations in this thesis were based on data reported by companies - owners and manufacturers in official open sources. Three companies were selected for comparison, which CO_2 emissions data was published in different years: RBIEP, conventional recovery boiler, and gas boiler. The implementation of the thesis consisted of the following stages: data collecting, calculations, comparison.

Based on the results of the calculations, it was proved that recovery boilers with improved energy production have much higher power production and lower amount of CO_2 emissions. Also, it was demonstrated that technologies used in such boilers allow decreasing the volume of other emissions into the atmosphere that makes pulp and paper industry production more environmentally friendly.

Language
English

Pages 69
Appendices 1
Pages of Appendices 1

Keywords
Recovery Boiler, emissions, energy, green technology, sustainable development

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GLOSSARY

CO_2 bio carbon dioxide emission from wood-based fuels

CO_2 fuel carbon dioxide emission from fossil fuel

Best Available Technology the technology approved by legislators or regulators for meeting output standards for a particular process, such as pollution abatement or pasteurization

Black liquor cooking solution formed in the pulp and paper industry, containing alkali, as well as other chemicals used in alkaline methods of cooking fibrous semi-finished products

Dissolving tank unit, where smelt is combined with white liquor, forming green liquor

Electrostatic precipitator device in which the cleaning of gases from aerosol, solid or liquid particles occurs under impact of electrical energy

Emission factor coefficient defining relation between activity data and GHG emissions

GHG-Emissions carbon dioxide, methane, ozone, nitrous oxide, hexafluoride, halocarbons, which in the atmosphere trap infrared radiation from the Earth, which can affect the Earth's climate ultimately

Green liquor green solution formed by dissolving inorganic water, which is obtained after burning black liquor in a regeneration furnace

Kraft black liquor the by-product from the kraft pulping process after pulping is completed

Lignin complex polymer compound contained in the cells of vascular plants

Recovery boiler high-temperature heat-technological installation, in the furnaces of which reactions are carried out aimed at restoring the chemical activity of the mineral part and burning out organic substances contained in the liquor. The heat of combustion of which is used to generate steam

Recovery Boiler with Improved Energy Production improved version of classic recovery boiler, implementing innovative technologies for increasing power-to-heat ratio and decreasing emissions

Scrubber industrial unit used to clean the exhaust polluted air from various impurities

Smelt molten inorganic chemicals, which are formed during the combustion of sulfate liquor with a high content of alkaline compounds in the reducing zone of furnace

White liquor strongly alkaline solution mainly of sodium hydroxide and sodium sulfide, used in a process of separation of lignin and hemicellulose from cellulose fiber

ACRONYMS

$(CH_3)_2S_2$ Dimethyl disulphide

$(CH_3)_2S$ Dimethyl sulphide

CH_3SH Methyl mercaptan

CO_2 Carbon dioxide

CO Carbon monooxide

C Carbon

H_2O Water

H_2S Hydrogen sulfide

N_2 Nitrogen

NH_3 Ammonia

NO_2 Nitric dioxide

NO_x Nitrogen oxides

NO Nitric oxide

Na_2S Sodium sulfide

Na_2 Sodium

O_2 Oxygen

SO_2 Sulfur dioxide

S Sulfur

ADt Air Dry Ton

BAT Best Available Technology

CHP Combined Heat and Power

CNCG Concentrated Non-Condensable Gases

CO2/ADt Carbon dioxide per Air Dry Ton

DNCG Diluted Non-Condensable Gases

DS Dry Solids

EPC Engineering, Procurement and Construction

ESP ElectroStatic Precipitator

NCG Non-condensible gas

RB Recovery Boiler

RBIEP Recovery Boiler with Improved Energy Production

SCR Selective Catalytic reduction

SNCR Selective non-Catalytic reduction

SOG stripper off gases

tds/day Tonnes of Dry Solids per Day

TRS Total Reduced Sulfur

1 INTRODUCTION

1.1 Background

The pulp and paper industry is one of the main drivers of the development of the timber industry nowadays. In doing so, the industry should not jeopardize efforts to preserve and maintain the environmental and recreational environment.

Paper is known to be made from cellulose. Cellulose, in turn, is obtained by cooking wood in huge boilers in a high-temperature alkaline environment and under high pressure. The basis for the production of pulp and paper products is deep thermal and chemical processing of wood. Today, pulp and paper industry enterprises are actively modernizing their facilities, using the latest technologies. (Promzn 2021.)

Product manufacturers are implementing solutions for automation and service, rational use of natural resources, and reduction of environmental, industrial and fire risks in production. Modern pulp and paper enterprises base their business strategy on the use of technologies that help preserve the environment. Nowhere is this more important than in the recovery boiler.

The main purpose of recovery boiler is to restore the chemical activity of the mineral part of the liquor, and the production of steam for use in the technological cycle of cellulose production was only auxiliary. Now, the energy generated from the black liquor stream in a modern recovery boilers is directed to reduce operating costs through energy efficiency, to build up mill own energy potential and use it as efficiently as possible. (KnowPulp 2021.)

In addition to recovering and recycling cooking chemicals in modern RBIEPs are produced clean steam and condensate for mill processes and energy production. Steam has become an essential modern energy source for thermal processes. Steam has significant advantages that make it an irreplaceable source of energy. (KnowPulp 2021.)

RBIEPs help pulp producers to be energetically self-sufficient and increase surplus steam and electricity production to provide biomass-based energy for public networks.

Benefits of Recovery Boiler with Improved Energy Production (Andritz Oy 2020a):

- High availability

- Reliable and safe operation
- Improved energy self-sufficiency
- Potential to generate green energy
- Less CO2 emissions per unit of electricity produced then in conventional recovery boilers
- Low NOX, CO, SO2 and TRS to the atmosphere emissions

1.2 Aim of study

The aim of the study is to analyse boilers' technologies for the production of clean energy. It is necessary to compile a more complete picture of available technologies and their advantages and disadvantages. Recovery Boiler with Improved Energy Production can produce more energy than steam boiler, using different kind of fuels. In thesis will be compared power to emission ratio for RBIEP, convention recovery boiler, biomass- and fossil fuel boilers. It will also review how RBIEPs can not only generate more energy, but also significantly reduce emissions to atmosphere.

This work presents the possibility of efficient combustion of Diluted Non-Condensable Gases (DNCG) collected from a pulp mill together with dissolution tank ventilation gases in a RBIEP to significantly reduce mill odours as air emissions. In the thesis, the principles of RBIEP operation are examined, their impact on the environment, as well as the amount of produced emissions.

In RBIEPs capital costs are reduced. The specific fuel consumption for electricity generation in steam turbine plants decreases with an increased capacity liquor combustion and steam parameters. Also as steam is used as a heat carrier - technological processes are intensified. One of the thesis targets is to prove a achieving of sustainable developments goals building boilers with such technology.

The key moments to study are principles of RBIEP work, and analyse impact to environmental, sources, amounts and ways of utilizations of emissions.

2 CONVENTIONAL RECOVERY BOILERS

Recovery Boiler (RB) is a power engineering unit, the main task of which is highly efficient chemical recovery, while economically burning the liquor. Waste black liquor containing lignin is burned in the furnace of the recovery boiler. This not only saves production resources, but also significantly reduces harmful emissions into the environment. Recovery Boiler is one of the main elements of the equipment of a pulp and paper mill complex. It allows to recover inorganic chemicals of cooking process, presented in the black liquor, by combustion process (reduction). At the same time organic matter in the black liquor is burned in the furnace producing high-temperature steam, that in turn can be used for energy production. (Kawasaki 2021b.)

2.1 Role in the pulp mill

Main tasks, performed by recovery boiler in the pulp mill:

- *Recovery of chemicals* from black liquor through combustion (reduction). During this process Na2S is reduced and green liquor is produced. It is used later for cooking chemical preparation. (SPb STUPP 2015, 1.)
  Reduction cycle can be seen on Figure 1.

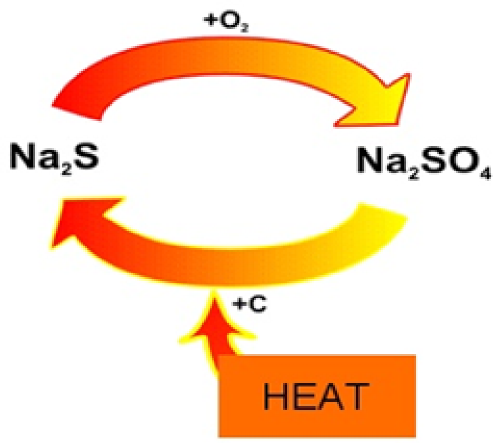

Figure 1: Reduction cycle (Andritz Oy 2020b)

- *Recovery of energy*. At a pulp mill, the liquor leftovers from the cooking liquor in the manufacture of wood pulp is concentrated and burned in a recovery boiler in the presence of biogenic fuels. In this case, the thermal energy of the waste gases formed during combustion is taken away, and, optionally, can be converted into electrical energy. (SPb STUPP 2015, 1.)

- Pulp mill *emissions reduction*. The production of cellulose by the sulfate method leads to the formation of foul-smelling sulfur-containing gases (methyl mercaptan, etc.), the presence of which, even in small quantities, is well-felt near such enterprises. These foul-smelling gases can be burned in boilers. Other unwanted air emissions include soot (carbon particles) and gas and dust emissions, which can be removed with electrostatic dust collectors (electrostatic precipitators). (Andritz Oy 2020b.)

- *Combustion of difficult (waste) streams* that are hazardous and/or harmful to environment. (Andritz Oy 2020b.)

2.2 Emissions in the recovery boilers

Recovery boiler is one of the sources of emission of pollutants into the air in pulp and paper mill. During its operation, sulfur dioxide, solid particles (mainly sodium sulfate and sodium carbonate), nitrogen oxides and hydrogen sulphide that are not burned, enter the atmospheric air. (Smorodin et al. 2010, 69.)

Figure 2 shows how the standard pulp process is going and where emission are born.

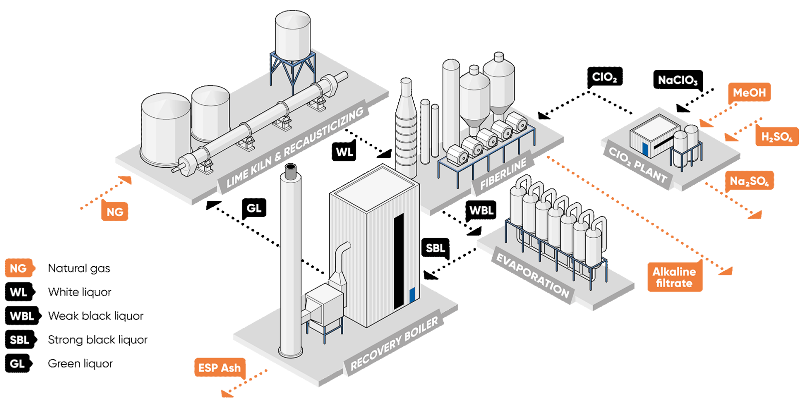

Figure 2: Standard pulp process (Andritz Oy 2020b)

The conventional recovery boiler is the emitter of gaseous emissions at the pulp mill. An example of data on the composition of emissions of pollutants into the atmospheric air from a conventional recovery boiler is given in Table 1. The usual solvent emissions are: *SO2 < 10 mg/m3(n)*, *TRS as H2S < 25 mg/m3(n)*, *dust*. The gas flow is typically around 6000-9000 m3/t of pulp, and the steam production process requires 13 to 18 GJ/t of cellulose. In case of hardwood use these values are higher. (Minpriroda of the Republic of Belarus 2016, 30.)

Table 1: Composition of emissions into the air from the RB in kg/DS and gas flow 6000-9000 m3/t of cellulose

Sulphur dioxide		
without scrubber, dry residue 63-65%	100-800	mg / Nm3
	60-250	mg / MJ
	1-4	kg / DS
with scrubber, dry residue 63-65%	20-80	mg / Nm3
	10-25	mg / MJ
	0,1-0,4	kg /DS
without scrubber, dry residue 72-80%	10-100	mg / Nm3
	12-30	mg / MJ
	0,2-0,5	kg /DS
Hydrogen sulphide		
about 90% of the time	<10	mg / Nm3
	0,05	kg / DS
short term	over	
Nitrogen oxides (in terms of NO2)	100-260	mg / Nm3
	50-80	mg / MJ
	0,6-1,8	kg / DS
Dust	10-200	mg / Nm3
after using an electrostatic precipitator	0,1-1,8	kg / DS

In case of mills, located in European Union, there is the Industrial Emissions Directive (2010/75 / EU), which obliges industry to meet agreed emission targets. Figures 3, 4, 5 present BAT values on the basis of the EU ITS (Official Journal of the European Union 2014, 26-27).

Parameter	Dust abatement system	Yearly average mg/Nm^3 at 6 % O_2	Yearly average kg dust/ADt
Dust	New or major refurbishment	10 – 25	0,02 – 0,20
	Existing	10 – 40 (1)	0,02 — 0,3 (1)

(1) For an existing recovery boiler equipped with an ESP approaching the end of its operational life, emission levels may increase over time up to 50 mg/Nm^3 (corresponding to 0,4 kg/ADt).

Figure 3: BAT-associated emission levels for dust emissions from a recovery boiler

Parameter		Yearly average (¹) mg/Nm^3 at 6 % O_2	Yearly average (¹) kg NO_x/ADt
NO_x	Softwood	120 – 200 (²)	DS < 75 %: 0,8 – 1,4 DS 75 – 83 % (³): 1,0 – 1,6
	Hardwood	120 – 200 (²)	DS < 75 %: 0,8 – 1,4 DS 75 – 83 % (³): 1,0 – 1,7

(¹) Increasing the DS content of the black liquor results in lower SO_2 emissions and higher NO_x emissions. Due to this, a recovery boiler with low emission levels for SO_2, may be on the higher end of the range for NO_x and vice versa.
(²) The actual NO_x emission level of a recovery boiler depends on the DS content and the nitrogen content of the black liquor, and the amount and combination of NCG and other nitrogen containing flows (e.g. dissolving tank vent gas, methanol separated from the condensate, biosludge) burnt. The higher the DS content, the nitrogen content in the black liquor, and the amount of NCG and other nitrogen containing flows burnt, the closer the emissions will be to the upper end of the BAT-AEL range.
(³) If a recovery boiler were to burn black liquor with a DS > 83 %, then NO_x emission levels should be reconsidered on a case-by-case basis.
DS = dry solid content of black liquor.

Figure 4: BAT-associated emission levels for NO_x emissions from a recovery boiler

Parameter		Daily average (¹) (²) mg/Nm^3 at 6 % O_2	Yearly average (¹) mg/Nm^3 at 6 % O_2	Yearly average (¹) kg S/ADt
SO_2	DS < 75 %	10 – 70	5 – 50	—
	DS 75 – 83 % (³)	10 – 50	5 – 25	—
Total reduced sulphur (TRS)		1 – 10 (⁴)	1 – 5	—
Gaseous S (TRS-S + SO_2-S)	DS < 75 %	—	—	0,03 – 0,17
	DS 75 – 83 % (³)			0,03 – 0,13

(¹) Increasing the DS content of the black liquor results in lower SO_2 emissions and higher NO_x emissions. Due to this, a recovery boiler with low emission levels for SO_2, may be on the higher end of the range for NO_x and vice versa.
(²) BAT-AELs do not cover periods during which the recovery boiler is run on a DS content much lower than the normal DS content due to shut down or maintenance of the black liquor concentration plant.
(³) If a recovery boiler were to burn black liquor with a DS > 83 %, then SO_2 and gaseous S emission levels should be reconsidered on a case-by-case basis.
(⁴) The range is applicable without the incineration of odorous strong gases.
DS = dry solid content of the black liquor.

Figure 5: BAT-associated emission levels for SO_2 and TRS emissions from a recovery boiler

Figure 6 shows the main inorganic reactions taking place in the recovery boiler, as well as the places where that reactions take place. A standard recovery boiler has an oxidation zone at the top and a recovery zone at the bottom. Strong black liquor is fed through one or more nozzles to the recovery zone. Combustion air is supplied at three different levels. (Minpriroda of the Republic of Belarus 2016, 31.)

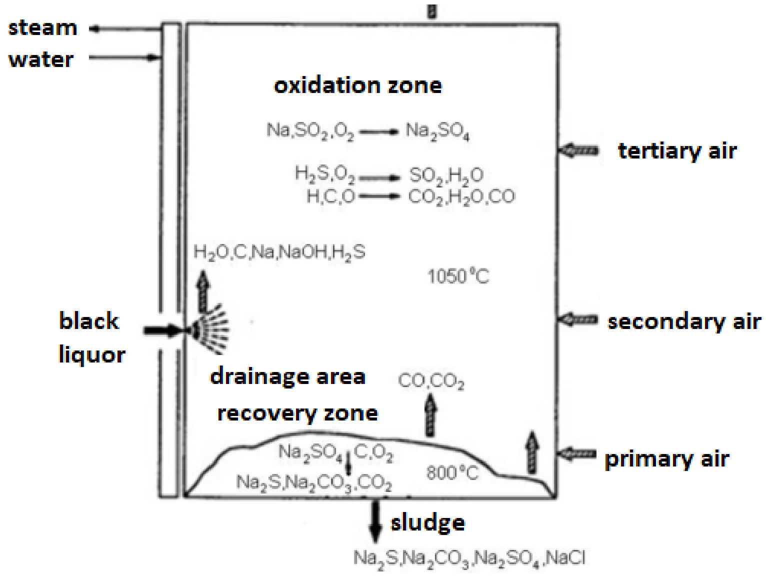

Figure 6: Main inorganic reactions occurring in the recovery boiler (Minpriroda of the Republic of Belarus 2016, 31)

Black liquor is regarded as a high-ash, low-calorie fuel with a high moisture content. From a thermal engineering point of view, black liquor entering the recovery boiler furnace with a concentration of 55 ... 65% of dry matter is a poor fuel. Its burning reaction, when happening spontaneously, is too slow and does not produce enough heat for self-maintenance. General combustion process requires addition of heat and air (oxygen) to liquor droplets. Heat is necessary to dry and de-volatilize liquor droplets and air is needed to oxidize combustible material. For that purpose, auxiliary burners are used. They allow to reach ignition temperature of air and black liquor. (Sivakov et al. 2015, 61.)

There are different techniques and methods, used to decrease emissions. For example, the black liquor is evaporated (concentrated) before further processing. After evaporation, concentrated black liquor contains about 65% solids. Approximately one third of the dry matter in it is inorganic compounds, and two thirds are dissolved organic matter (Sivakov et al. 2015, 16). The purpose of the evaporation (concentration) of the lye is to increase the proportion of dry residue fed to the recovery boiler to obtain a larger volume of steam. By installing additional equipment, the proportion of dry residue can be increased to 75-80%. An increase in the content of dry residue in black liquor from 65-70% to 80-85% changes the material and energy balances and combustion conditions in the recovery boiler (Vakkilainen 2005, 1-7, 2–10). The flue gas flow decreases as the amount of water entering the furnace decreases. As the solids content increases, the combustion temperature rises and causes more evaporation of sodium, which then reacts with sulfur and reduces sulfur emissions from the recovery boiler. However, the disadvantage of raising the temperature is the increased emissions of nitrogen oxides. Reducing NO_x emissions, in turn, can be achieved by modifying the air supply and optimizing combustion conditions. (Vakkilainen 2005, 9-11.)

Another approach to emissions reduction is equipping water recovery boiler with an electrostatic precipitator, that allows to capture a large amount of solid particles (dust, mainly Na2SO4) from flue gases. The captured solids are reused to make strong black liquor (Fedorova 2020, 21, 46). To reduce SO_2 emissions, the recovery boiler is equipped with a scrubber operating at a pH value of 6-7. The pH is adjusted by adding sodium hydroxide (NaOH), weak liquor, or oxidized white liquor. As the pH rises, hydrogen sulfide is captured, and carbon dioxide is absorbed and neutralized with alkali. Surplus liquor from the scrubber is recycled to the process, usually forming white liquor. (Andritz Oy 2020b.)

Developments have taken place and will continue to take place, but it is impossible to get rid of emissions completely, however proper design and operation of a recovery boiler can minimize harmful emissions.

3 RECOVERY BOILERS WITH IMPROVED ENERGY PRODUCTION

Typical Recovery Boiler do not produce enough energy to cover nowadays requirements. To resolve this problem the Recovery Boiler with Improved Energy Production (RBIEP) concept was developed. In simple words, it is a Recovery Boiler with addition of different up-to-date equipments and technologies that increase the chemical recovery and energy generation. New methodologies and innovative facilities makes it possible to increase power generation efficiency a way further it could be possible with just steam parameters improvements. Concept of RBIEP produce not only environmental benefits, but also yield a noticeable economical savings. That makes them very attractive from business profit point of view.

3.1 World coverage

Nowadays there are multiple RBIEPs all over the world. Newly built mills are aiming to the use of Recovery Boilers with Improved Energy Production benefits from the start. However, even older RBs can be modernized to achieve high power-to-heat ratio:

- *RBIEP at Mondi Frantschach, South Austria* (fig. 7). In this mill stripper off gases (SOG) and Concentrated Non-Condensable Gases (CNCG) are burned in one burner, that allows to reduce fossil fuel usage. (Heinola et al. 2014, pp 23-25.)

Figure 7: RBIEP at Mondi Frantschach, South Austria (Andritz Oy 2020a)

- *RBIEP at Ružomberok, Slovakia* (fig. 8). Mondi pulp and paper in Ružomberok is one of the key pulp and paper mills Mondi Group. The installation of a new boiler will allow the company to fully meet its energy needs, and 94% of the energy will be generated from the use of renewable resources. (Teittinen et al. 2015, 44-45.)

Figure 8: RBIEP at Ružomberok, Slovakia (Andritz Oy 2020a)

- *RBIEP at Montes del Plata, Uruguay* (fig. 9). Montes del Plata Mill in south-west Uruguay is joint venture between Finnish Stora Enso and Chilean Arauco. Raw materials for production come from their own eucalyptus plantations in Uruguay. (Stora Enso 2021.)

Figure 9: RBIEP at Montes del Plata, Uruguay (Andritz Oy 2020a)

- *RBIEP at Suzano, Três Lagoas, Brazil*. The largest in Latin America and the second largest in the world.
- *RBIEP at SCA Östrand, Timrå, Sweden*. World's largest softwood pulp line.
- *RBIEP ITC's Bhadrachalam, India*. An existing pulp mill that is planned to be updated by 2021 with new recovery boilers.

- *RBIEP at Ust-Ilimsk, Russia*. An existing pulp mill actively developing, expanding and modernizing since 2017. (Andritz Oy 2019.)
- *RBIEP Guaíba pulp mill*. Located close to Porto Alegre in Rio Grande do Sul State, Brazil. According Valment's statement "no longer emits any hazardous or malodorous gases into the environment" (Valmet 2016).
- *RBIEP Suzano Pulp and Paper, Brazil*. This mill states strong targets for environment friendliness and sustainable development. (Suzano 2021.)
- *RBIEP bioproduct mill in Äänekoski, Finland*. The largest wood-processing bioproduct mill in the northern hemisphere. It was started in 2017, nominal capacity was reached in 2018. (Valmet 2021.)
- *RBIEP Segezha pulp mill, Russia*. Pulp and paper mill started to operate in 1939, passed several reconstruction cycles. Latest modernization project started in 2019. (Segezha Group 2021.)

RBIEPs are actively built in different parts of the world. There are both new mills projects and reconstructions of existing ones, involving upgrade and modernization of recovery boilers currently in use.

3.2 Studied new generation Recovery Boilers

For writing the thesis I studied common principals of recover boilers operation, emissions and energy production. I have also reviewed available information on following paper mills, implementing Recovery Boiler with Improved Energy Production.

3.2.1 Mondi Ružomberok in Slovakia

This is the largest pulp and paper mill in Slovakia. Mondi Group invested a lot into its modernization and reconstruction during last years. Currently it is the largest investment project in the history of SCP Mondi. One of the latest improvements is installation of new recovery system. It was delivered on an EPC basis, with engineering done by Andritz and civil construction - by Mondi.

We knew this would help us increase energy self-sufficiency while debottlenecking our recovery operations. - Vladimir Krajči, Pulp Operations Manager, Teittinen et al. 2015, 44-45

Implementing new Recovery Boiler with Improved Energy Production (RB3) allowed to increase the overall energy production. That in turn lead to energy self-sufficiency and much lower emission footprint of the mill. New Recovery Boiler has capacity of 1750 tds/day and produce 87.7 kg/s of steam at 495 °C and 96 bar. Used black liquor is reported to be low on chlorides in exchange of higher potassium levels. (Teittinen et al. 2015, 44-45.)

For testing period, recovery boiler was operating with 115% of capacity. Under normal conditions it operates in 90-95% range. Thus majority of the time installation work under maximum possible load, that decrease overall emissions, but still it is enough to fulfil mill's energy requirements. (Teittinen et al. 2015, 44-45.)

3.2.2 Ilim Group's "Big Ust-Ilimsk Project", Russia

This RBIEP is currently under implementation as a part of large investment project on construction of a new pulp and cardboard mill in Ust-Ilimsk. Planned end of project implementation is 2022. However, the boiler is scheduled to start up already in 2021. The capacity of new RBIEP will be 1950 tons of absolutely dry matter per day. (Andritz Oy 2019.)

Ust-Ilimsk mill's RBIEP is designed to reduce emissions into the atmosphere and significantly weaken the impact on environment (Andritz Oy 2019):

- highly efficient two-chamber electrostatic precipitator for collecting dust, that will provide a dust concentration in the emission of no more than 50 mg / Nm3;
- additional combustion systems, including a backup burner, to ensure burning of highly concentrated gases;
- provisioning with an efficient thermal energy recovery system, which will save resources;
- the dry matter content in the black liquor supplied for combustion will be increased

up to at least 75% (due to the enhanced capacity of the equipment), which will in turn increase the efficiency of boiler unit.

In addition, the RBIEP will be equipped with a fully automated control system (including automatic controller of combustion) and online monitoring of technological processes states, which will ensure increased reliability and safety of production. (Andritz Oy 2019.)

3.2.3 Bioproduct mill in Äänekoski

The bioproduct mill in Äänekoski is next example of pulp and paper mill with RBIEP. It was greatly modernized during a process started in 2017. After reconstruction it is able to produce 1.3 million tonnes of pulp a year from 6.5 million cubic meters of wood. (Engström 2017.)

This mill is referred as a "bioproduct mill" due to the high standards of environmental and sustainability goals. The processes are stated not to use fossil fuels at all and consume only 10 m3 of water per tonne of pulp. Furthermore, Camilla Wikström, Mill Manager (Andritz Oy 2017, 21-27) stated:

> *We are proud to say that the Äänekoski mill is using the same environmental permit that was granted for the original mill it replaced – even though the mill is two and a half times bigger.*

This mill is a complete wood processing plant with three debarking and chipping lines, that are able to get both soft- and hardwood as an input. Bark is pressed with an innovative HQ-Press – which increases the dry solid content of the bark, that results in higher energy production on later process stages. Evaporation plant of the mill is has the highest capacity in Europe and is one of the largest re-causticizing plants in the world. (Engström 2017.)

3.2.4 Segezha pulp mill, Russia

This mill was built in 1939. Since that it went through several modernizations and reconstructions. As a result, currently it produces 375 000 tons of paper. In 2019, it initiated a project for next modernization, that should increase production up to 600-700 thousand tons of paper per year. This project involves installation of several new RBIEPs with updated electrostatic precipitators and the replacement of hot stage of the water economizer. After replacing the electrostatic precipitator, the efficiency of collecting solid particles at RB-2 will be 99.9%, which will significantly reduce the impact of mill on the atmosphere. Modernized boiler will reduce emissions of harmful substances into the atmosphere by 10 times compared to the previous volumes. Planned boiler capacity will be about 10 MW (Segezha Group 2021).

3.3 Principle of work

The main function of the RBIEP is to burn the organic portion of black liquor (a by-product of chemical pulping) in a heap or bed, supported by the furnace bottom. That releases energy, used to produce steam, and reduces the oxidized inorganic portion of the black liquor. Molten mineral chemicals in a layer known as melt are discharged into a water reservoir where they dissolve and regenerate as green liquor. The heat released as a result black liquor combustion is used in chemical and physical processes that take place with additional heat consumption, and the excess is used to generate steam and to heat water and air entering the boiler. (Kuparinen et al. 2019, 1216.)

The designs of boilers are very diverse. But all of them contain six main functional groups of equipment as shown on Figure 10 (Andritz Oy 2020b):

- black liquor preparation for combustion (increase the concentration)
- heating and air supply to the furnace (fans, guide vanes, air heaters, air ducts)
- furnace zone (liquor, fuel oil and air supply nozzles, screen tubes and protective plates, mounted inside the firebox)
- steam boiler (equipped with a furnace screen, scallop, convective tube bundle, superheater, drums, pipe cleaning devices, water and air economizers)
- cooling and cleaning of flue gases (gas ducts, ash pans, fans-smoke exhausters,

electrostatic precipitators, chimneys, equipment for thickening black liquor - venturi scrubbers, cascade evaporators)

- smelt pot (equipped with vertical or horizontal stirring device, heat trapping and chemical entrainment devices).

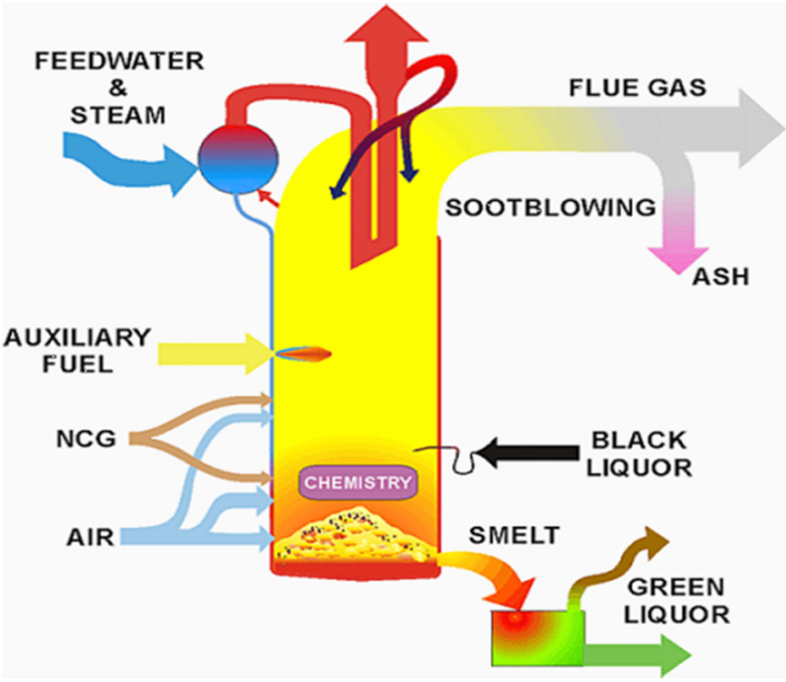

Figure 10: Processes in Recovery Boiler with Improved Energy Production (Andritz Oy 2020b)

The furnace is fed through the upper drum, where water enters the lower drum through the screen pipes, and then through the drain pipes it is supplied to the lower collectors of the furnace walls. Due to natural circulation, the steam-water mixture begins to rise along the front screen of the furnace back to the upper drum, which forms a slightly inclined ceiling of the furnace, where, with the help of a separation device, droplets of water and steam are separated from the steam-water mixture. Water goes to the "second circle", and steam enters the superheaters (Smorodin et al. 2018, p.7).

The evaporated black liquor is injected into the furnace of the recovery boiler using special nozzles. In the combustion chamber, as a result of the reaction of black liquor with air, a significant amount of thermal energy is released and smelt is formed, which flows from the lower part of the furnace along the smelting tap hole into the solvent tank, where it dissolves with weak white liquor, forming green liquor. The flue gases generated during combustion heat the walls of combustion chamber pipes, rise and flow from the furnace to superheaters and then to the convection zone. Driving force is caused by density difference between water in downcomers and water-steam mixture in furnace tubes. It can be enhanced by heating tubes or reduced by pressure increase. (Fedorova 2020, 20-22.)

Heat recovered from the flue gases is transferred to superheated steam, which is fed to a steam turbine to generate electricity. In addition, some of the steam is used in various technological processes for the production of cellulose as shown on Figure 11. (KnowPulp 2021.)

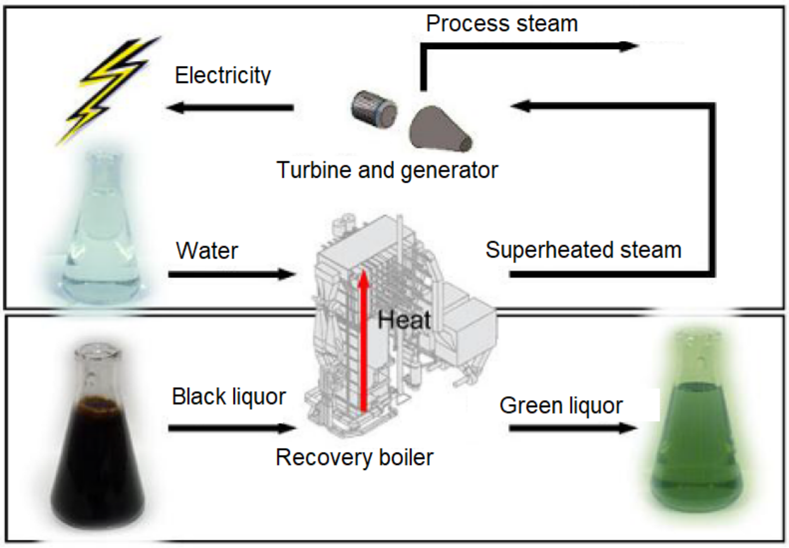

Figure 11: Recovery boiler generated heat usage (KnowPulp 2021)

Combustion is oxidizing of combustible material. Burning reaction can be accelerated by adding external heat to the process. If the reaction is so rapid that it produces more heat than it consumes, reaction maintain by itself (ignition temperature). To increase the heat of fuel working mass combustion, it is often used to supply additional fuel or fuel oil to the furnace. (Vakkilainen 2005, 9-27.)

Liquor, used in RBIEPs, has dry content increased from 65 to 80-85% of solids. Black liquor is injected into the recovery boiler from a height of 5...8 meters. For efficient combustion of liquor, additional air is supplied to the furnace. The air is introduced in several streams at different levels of the furnace height, having different temperatures and pressures as show on Figure 12 (Sivakov et al. 2015, 19-20, 26):

- **primary air** - lower level of the furnace. Main support of combustion process.
- **secondary air** - above the level of the primary air inlet but below the liquor spray nozzles. It must be adjusted so that the volatile and gaseous particles from the

black liquor mix optimally with the combustion air and do not leave the boiler unburned, which would of course reduce the efficiency of combustion process. An uneven or inefficient supply of secondary air produces particularly poor combustion results, clogs heating surfaces and increases emissions (pollutants) in the flue gas. In addition, volatile particles and chipping particles can very easily cause contamination of the surfaces in the heat recovery devices connected to the boiler. Any unregulated particles coming out of the boiler also increase unwanted and/or harmful emissions. (Smorodin et al. 2018, 5-8.)

– **tertiary air** - above the liquor spray nozzles. Allows complete combustion.

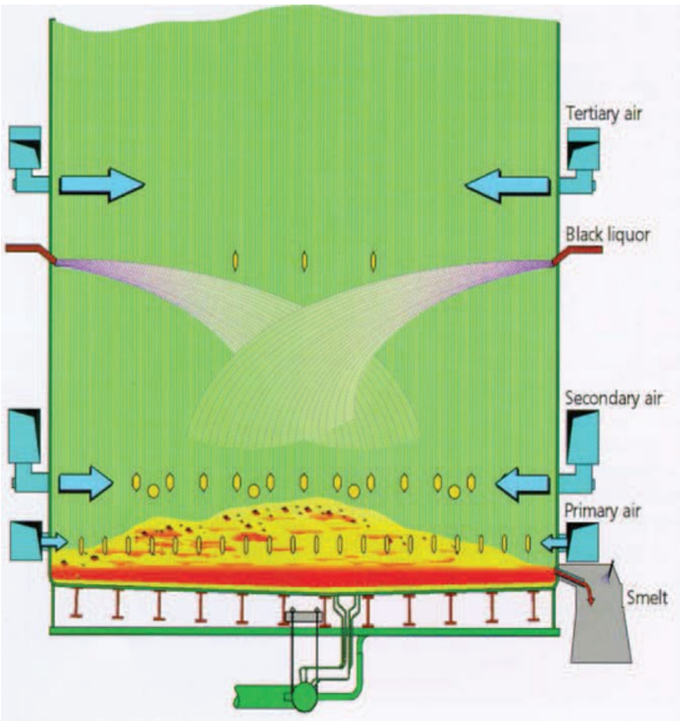

Figure 12: Air streams in furnace (Vakkilainen 2005, 4-9)

Air is usually introduced through several holes located in all four edges of the furnace. Number and size of the air nozzles as well as the height distribution of the air supply can vary. Air supply ensures fast mixing in the boiler. It is necessary to regulate the symmetry of combustion over the entire cross-sectional area of the boiler and, if necessary, adjust the air supply. (Smorodin et al. 2010, 66-68.)

One of the examples of improved air system is Vertical Air system (fig. 13), used in Andritz RBIEPs. It mixes the air, surrounding the combustion process. That increase the efficiency of recovery furnace operations. Another benefit is decrease in flue gases volumes, as furnace requires less excess air for operation. Lower amounts of gas results in lower power consumption by ducts operation equipments. And finally, reduced excess air leads to significantly lower NO_x emissions. (Andritz Oy 2020b.)

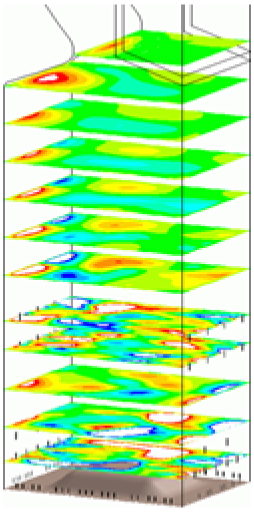

Figure 13: Vertical Air system (Andritz Oy 2020b)

Targets of using such air system are:

- Right amount air to right places
- Effective mixing
- Even flue gas flow profile in the furnace
- Optimum heat transfer in the furnace
- Combustion finalization with minimum amount of excess air

Some of the advantages of implementing such air systems are:

- Minimum carry-over
- High sulfur recovery
- Low emissions (NO_x)
- Good char bed control

Black liquor combustion forms the char bed at the bottom of the boiler, where complicated reactions occur. The smelt is drained from the boiler and is dissolved with weak white liquor to form green liquor, which contains the recovered chemicals. High pressure steam is generated from feed water by heat released from combustion reactions. (Andritz Oy 2020b.)

3.4 Emissions to air

Recovery boiler plays an essential role in the production of pulp and paper products. The quality of its work depends on how environmentally friendly the process of chemical regeneration during cooking sulfate pulp will be. The Recovery Boiler with Improved Energy Production is manufactured taking into account global environmental standards and the Best Available Technology (BAT) in a field of ecology. Reducing the burden on the environment is a global priority. (Official Journal of the European Union 2014, 25-27.)

The production of sulfate pulp is associated with the formation of significant quantities of gas emissions containing toxic and foul-smelling compounds. One of the main sources of emissions is RBIEP, although the concentrations of odorous compounds in flue gases are usually low. Foul-smelling gases are divided into concentrated (above 5 g / m3) and diluted (<0.5 g / m3). Diluted heating gas, for example, from screening, washing of pulp, solvent tank and ventilation of various containers containing black liquor, etc., with a sulfur content of 0.2-0.5 kg/DS (Ministry of the Environment of Finland 1997, 46).

Foul-smelling sulfur-containing gases, formed mainly during the drying and pyrolysis of black liquor in the furnace of Recovery Boiler with Improved Energy Production (Smorodin et al. 2010, 69):

- Hydrogen sulfide (H_2S)
- Methyl mercaptan (CH_3SH)
- Dimethyl sulphide ($(CH_3)_2S$)
- Dimethyl disulphide ($(CH_3)_2S_2$)

The optimal combustion mode allows to minimize the release of foul-smelling compounds from the firebox. In RBIEPs performs efficient combustion of all Diluted Non-Condensable Gases (DNCG) collected from a pulp mill together with dissolution tank ventilation gases. However, the use of a gas-contact evaporator in the technological scheme leads to a manifold increase in the emissions of hydrogen sulfide and methyl mercaptan. (Andritz Oy 2020a.)

A tables with real emission data for RBIEP and for non-RBIEP industrial steam boilers are presented in Appendix 1.

3.4.1 Sulfur dioxide, SO_2

It is colourless gas with a specific sharp odour. Toxic with inhalation. Sulfur dioxide is one of the main air pollutants. It is formed during the combustion of sulfur, which is usually found in natural fuels. SO_2 is harmful to plants, and is a leading cause of acid rain. However, it is not treated as part of a GHG-Emissions. (LLC "Laboratory Measurements and Labor Protection" 2021.)

Sulfur emissions from a RBIEP depend on the following factors (Andritz Oy 2020b):

– temperature in different zones, depending on the concentration of dry residue in black liquor and the amount of incoming air

– the ratio of sulfur and sodium (S / Na_2) in the liquor (sulphidity). A high sulphidity index means that the released sodium is not enough to bind the sulfur, and therefore the excess sulfur enters the atmospheric air as SO_2. The high solids content of the black liquor compensates this effect

– air masses - excess air volume, primary air temperature and combustion air distribution

– uniform distribution of black liquor throughout the recovery furnace

– load on the boiler - operation of the RB in an overloaded mode has a negative impact on the emission parameters

To reduce SO_2 emissions, the recovery boiler (including RBIEP) is equipped with a scrubber, operating at a pH value of 6-7. The pH is adjusted by adding sodium hydroxide (NaOH), weak liquor, or oxidized white liquor. As the pH rises, hydrogen sulfide is captured, and carbon dioxide is absorbed and neutralized with alkali. Surplus liquor from the scrubber is processed and recycled into other chemicals, usually white liquor. (Andritz Oy 2020b.)

The amount of sulfur dioxide SO_2 is affected by (Andritz Oy 2020b):

– Low dry matter content. Figure 14 shows how SO_2 emissions depend on dry matter content. It can be seen that as the dry matter content increases, the emissions decrease;

– Cold furnace. Dependency of SO_2 emissions on furnace temperature can be seen on Figure 15;

– High sulfur content (S) in black liquor;

– High sulphidity level (S / Na);

– Low sodium content (Na) in black liquor;

– Poor combustion of odorous gases.

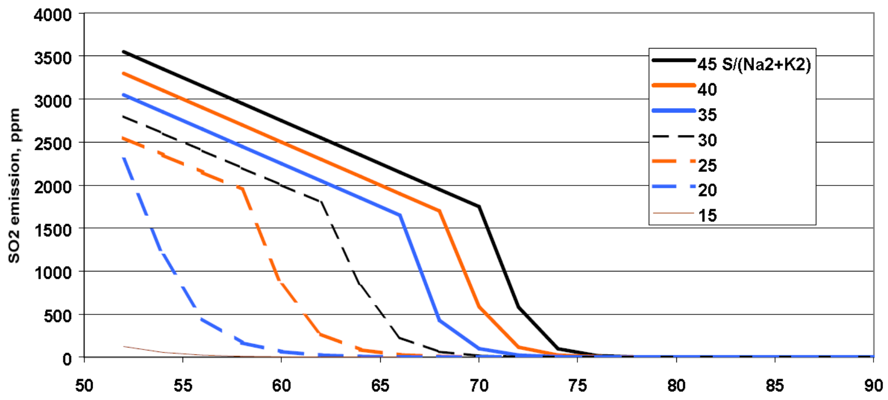

Figure 14: SO_2 emissions by dry matter fraction (Vakkilainen 2005, figure 11-9)

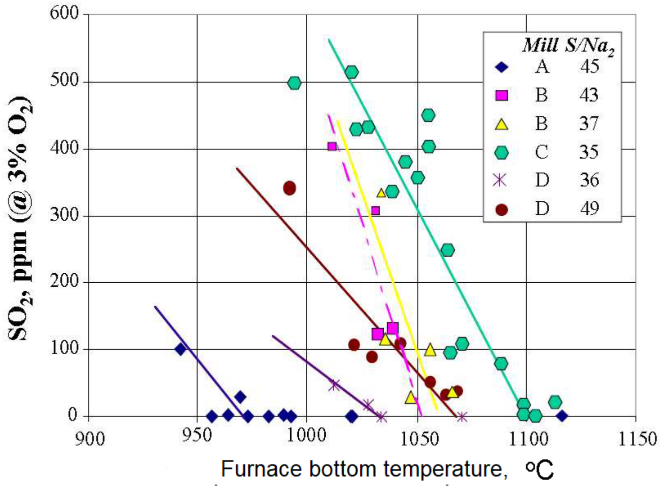

Figure 15: SO_2 emission as a function of furnace temperature (Vakkilainen 2005, figure 8-24)

SO_2 emissions' has several negative consequences for processes and equipment (Andritz Oy 2020b):

– Sulfur loss, i.e. the chemical is removed from the balance sheet and must be replaced to keep chemical processes

– The pH of ash decreases

- Possibility of boiler fouling
- Increased soot vapour consumption
- Increased corrosion

One of the techniques, which RBIEP implements to minimize the amount of free gaseous sulfur in the furnace is keeping temperature of lower part of the furnace at 1000-1200 C (fig. 16). In this case sodium is released / gasified (Na or Na_2CO_3) and reacts with SO_2 to form sodium sulphate Na_2SO_4 (1) (Sivakov et al. 2015, table 13).

$$SO_2 + \frac{1}{2} O_2 + Na_2CO_3 \longrightarrow Na_2SO_4 + CO_2 \quad (1)$$

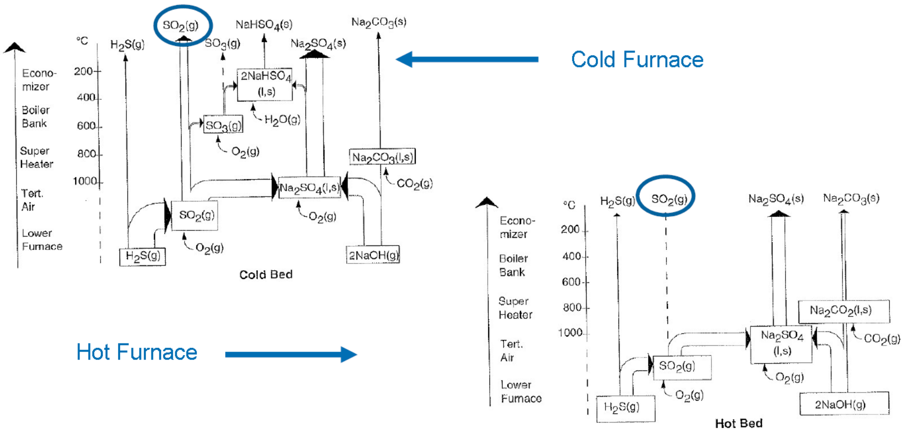

Figure 16: SO_2 emissions depending on the furnace temperature (Andritz Oy 2020b)

The temperature at furnace bottom is affected (as long as there is a heap) by (Andritz Oy 2020b):

- liquor spraying (dry matter, spray pressure, spray size and spray temperature)
- secondary air amount of and distribution location
- primary air amount
- combustion air temperature

3.4.2 Nitrogen oxides, NO_x

Term NO_x relates to two nitrogen oxides gases - nitric oxide (NO) and nitrogen dioxide (NO_2). Nitric oxide can form smog (ground-level ozone), which damages vegetation and reduces yields. Reacts with other chemicals, forming a wide variety of toxic products. When nitric oxide and sulfur dioxide react with other constituents in the air, acid rain is formed. Inhalation of the pure gases is rapidly fatal. NO_x are formed during the oxidation of nitrogen-containing substances present in the fuel in the flame zone. The concentration of fuel oxides can reach significant sizes if the content of nitrogen-containing substances in the fuel exceeds 0.1% by weight. As a rule, this only applies to liquid and solid fuels. (UCAR 2021.)

Nitrogen emissions from the Recovery Boiler with Improved Energy Production is mainly nitrogen oxides (NO). The formation of nitrogen oxides in the RBIEP mostly depends on the nitrogen concentration in the black liquor and amount of excess oxygen. The formation of nitrogen oxides at low oxygen concentrations ranges from 1 to 2 kg/t of cellulose. An increase in oxygen concentration by 1.5-2.5% can step-up nitrogen oxide emissions by about 20% as shown on Figure 17. (Andritz Oy 2020b.)

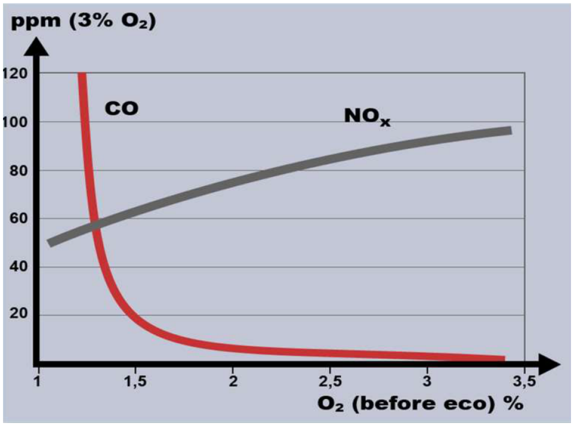

Figure 17: NO_x / CO, Effect of oxygen concentration and air phasing (Andritz Oy 2020b)

An increase in the proportion of solid sludge from 65 to 75% can also increment nitrogen oxide emissions by up to another 20% (fig. 18). Hardwood has a higher nitrogen content than softwood, which in turn can increase NO_x emissions by about 10%. The amount of nitrogen oxides in emissions is affected by (Andritz Oy 2020b):

- nitrogen content of the liquor (in wood typically 0.05. . . 0.15% of mass)
- low air phasing and boiler load

- use soft- or hardwood as a source. Hardwood typically has higher NO_x emissions

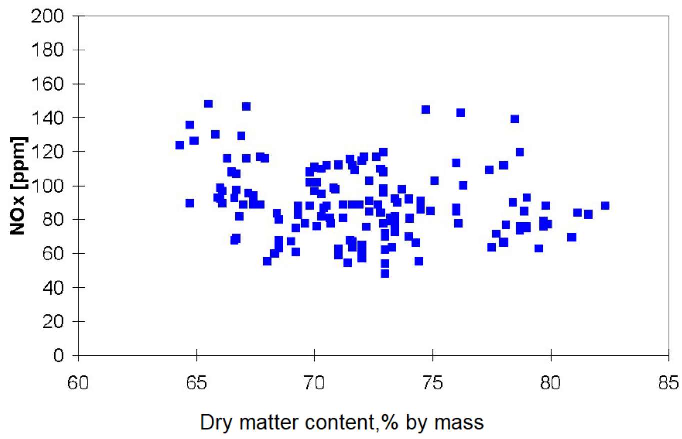

Figure 18: Dependency of NO_x emissions from dry matter content (Vakkilainen 2005, figure 11-4)

Additionally, similar to SO_2, NO_x emissions depend on furnace temperature (fig. 19).

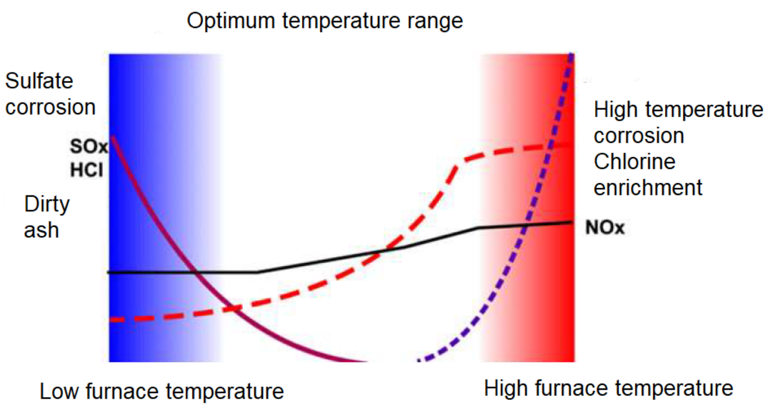

Figure 19: Temperature impact on furnace process (Andritz Oy 2020b)

It appears that recent changes in recovery boilers have in practice increased NO_x emissions. Due to the specifics of processes alterations, made to decrease one emissions increase other ones. For example, growth in the dry matter fraction and the combustion of odorous gases leads to lower CO and SO_2 in trade of higher NO_x. Reduction of NO_x emissions can be achieved by following (Andritz Oy 2020b):

- optimizing air volumes
- optimizing liquor spraying characteristics
- correct air phasing (to make mixing of fuel with air more effective)
- use of SNCR, SCR and NO_x scrubbers

- decreasing the load of the boiler

Effect of RBIEP load on NO_x emissions: lower load, lower temperature and better combustion control (e.g. longer delay times with flue gas) - decrease emissions (Vakkilainen 2005, 9-14 - 9-18).

Recovery Boiler with Improved Energy Production implements several settings, that directly influence NO_x emissions (Andritz Oy 2020b):

- Low oxygen or a little CO emissions
- Phases the air supply, to inject as much as possible of it from the top
- Big drops of black liquor

Opportunities to reduce NO_x emissions in RBIEP, that are currently under development (Andritz Oy 2020b):

- Priority actions
  - Combustion air phasing - should give emission reduction up to 30%
- Secondary actions
  - Selective non-Catalytic reduction (SNCR) - reduction by 30 - 50%
  - NO_x scrubber - reduction by 60 - 65%
  - Selective Catalytic reduction (SCR) - reduction by 80 - 90%
  - NH_3 injection

3.4.3 Carbon monoxide, CO

This is a colourless, odourless, tasteless, flammable and highly toxic gas. It is dangerous for any animal using hemoglobin as an oxygen carrier.

Any process in which incomplete combustion of organic material can occur is a potential source of carbon monoxide. In the furnace, air passes through the coke bed. The originally produced CO_2 is equilibrated with the remaining hot carbon to form CO (Vakkilainen 2005, 4-7):

$$O_2 + 2\,C \longrightarrow 2\,CO \qquad (2)$$

The appearance of CO emissions in RBIEP processes is caused by poor air mixing and insufficient combustion as shown on Figure 20 (Andritz Oy 2020b).

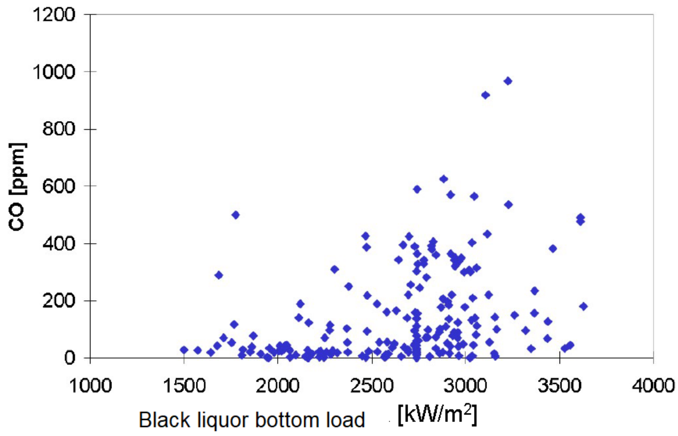

Figure 20: Carbon monoxide CO emissions in Recovery Boiler with Improved Energy Production (Vakkilainen 2005, figure 11-2)

One of the reasons for emissions of carbon monoxide from recovery boilers is the operation of the boiler above its rated capacity, which leads to the inability to withstand oxidation conditions. High furnace temperature and long delay time reduce emissions. However, reducing CO in turn increases NO_x and TRS emissions. (Andritz Oy 2020b.)

3.4.4 Carbon dioxide, CO_2

Carbon dioxide is a low-toxic gas, odourless and colourless under normal conditions. It is released into the atmosphere from the combustion of fossil fuels, solid waste, trees and other biomaterials, as well as through a number of chemical reactions. Carbon dioxide forms the "greenhouse effect" and affects the climate. The rapid rise in levels of CO_2 and other gases in the atmosphere can lead to unpredictable climatic changes. Therefore, reducing carbon dioxide emissions is essential. (Aniskov 2021.)

CO_2 emissions are distinguish to ones from biomass (CO_2 bio) and fossil fuel (CO_2 fuel). Black liquor is a biofuel. Consequently, the main substance emitted into the atmosphere is neutral (from the standpoint of the Kyoto Protocol) CO_2. It is assumed that carbon dioxide produced from Black liquor burning is re-absorbed back to organic matter in forests (Vakkilainen 2005, 11-3). The proportion of carbon dioxide released during combustion is equal to that absorbed by trees during photosynthesis, and therefore it returns to the atmosphere without exceeding the carbon content. Thus, biomass combustion does not increase the greenhouse effect. Opposite to CO_2 fuel that increase overall amount of carbon dioxide in the environment. In a context of RBIEP operations, fossil fuels can be used as auxiliary energy source during startup shutdown, upsets or for extra steam production. According Kuparinen et al. 2019, 1216 approximate levels of CO_2 emissions are:

- *CO_2 bio*: 1600–2400 kg CO2/ADt
- *CO_2 fuel*: 10–20 kg CO2/ADt

CO2 fuel emissions can eventually increase due to sudden upsets or equipment failures, when side energy sources are required.

CO_2 is formed in kraft pulp mills primarily during combustion, when carbon (C) in the fuel oxidizes ($C + O_2 \longrightarrow CO_2$). Emitted CO_2 leaves the stack altogether with the flue gas. (Sivakov et al. 2015, 33, 49.)

The main CO_2 sources at pulp and paper mill are recovery and biomass boilers, and the lime kiln (fig. 21). Another source is a process of destruction Non-condensible gas (NCG) with several vents, but it is a negligible one. In most cases the main (or even only one) source of CO_2 fuel is lime kiln. (Kuparinen et al. 2019, 1216.)

Figure 21 shows a schematic diagram of a kraft pulp mill with key points of CO_2 emissions.

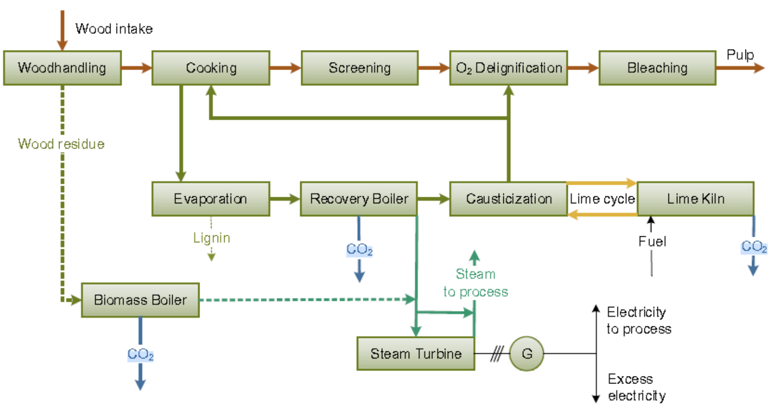

Figure 21: CO_2 removal streams (Kuparinen et al. 2019, 1216)

3.4.5 Dust

These are very small particles that are harmful to health. Small enough dust pieces when inhaled may lead to irritation of the eyes, coughing, sneezing, hay fever and asthma attacks. In addition to that, dust formed by chemicals can lead to particular chemical-related health problems. In a context of RBIEP emissions, dust usually consists of sodium sulfate Na_2SO_4 (79%) and sodium carbonate Na_2CO_3 (21%) (Sivakov et al. 2015, 45).

The amount of dust emissions is affected by (Andritz Oy 2020b):

- dry matter content (fig. 22), with an increase in dry matter content, the amount of dust decreases
- furnace temperature
- boiler load
- electrostatic precipitator malfunction
- incorrect liquor supply (carry-over)

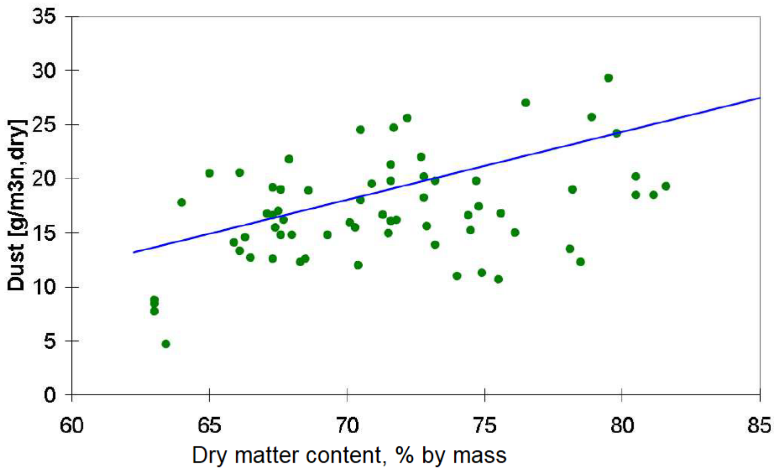

Figure 22: Dust emission after economizer (Andritz Oy 2020b)

In Recovery Boiler with Improved Energy Production electrostatic precipitators of new generation are installed. They provide almost one hundred percent cleaning of dust emissions: the degree of particulate matter capture should be 99.97%. It is achieved by use of unusual gas inlets and outlets - they are located on top of device, which results in upper shaking if content. (Sanaev 2011, 464.)

One of the general problems, connected to dust is caking of particles. RBIEPs implements scraper conveyors inside filter bins to overcome it. In case of dust particles in electrostatic precipitators, caking is eliminated with modelling the field strength. All scraped and filtered dust is returned back to the production cycle. Due to the high level of purification, almost pure vapour is released into the atmosphere. (Andritz Oy 2020b.)

3.5 Emissions' reduction

Recovery Boiler with Improved Energy Production concept was developed not only for power-to-heat ratio improvements, but also for decreasing environment impact from one of the main sources of emissions of the pulp and paper mills. Thus it implements multiple different methods and equipments used for emissions reduction in addition to burner and combustion process optimization. The work on further developments and improvements is supported by different initiatives originated from actors involved into pulp-and-paper industry.

3.5.1 Technical methods

Emission reduction-related common rules for RBIEPs are (Andritz Oy 2020b):

- **CO** - keep vents clean
- **NO_x** - last air level as high as possible
- **SO_2, TRS** - increase furnace temperature
- **DUST** - minimal amount of flue gas and working filters

Using different air dampers and air connections at distinct levels and locations. One of the ways to achieve this is implementation of multilevel air systems (fig. 23). Such implementations alter primary and secondary air flows, as well as improve nearby liquor airflow and double tertiary air volume. That results in low emissions through increased staging and higher air delivery marks. These systems significantly reduces the level of nitrogen oxides (NO_x), carbon monoxide (CO) and other harmful compounds. (Babcock and Wilcox 2008, 4.)

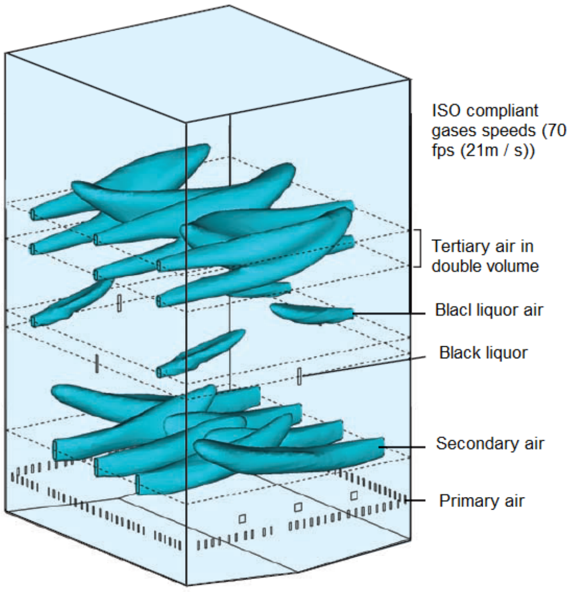

Figure 23: Multilevel air system (Babcock and Wilcox 2008, 4)

Alternating return of secondary air supply units minimize gas plume along the rear wall of the furnace, reducing CO emissions. Single-stage secondary blasting provides excellent control of combustion in the coke bed at both low and high solids content, which minimizes operational disturbances and gas fuel consumption. The level of the liquor air blast reduces dust entrainment above the liquor nozzles. Dual tertiary blast nozzles aligned with the liquor nozzles reduce particle entrainment, improve mixing and decrease overall emission levels, allowing for longer cycle times between washes. (Andritz Oy 2020b.)

Cleaning of flue gases in electrostatic precipitators. All RBIEPs are equipped with electrostatic filters, which are very reliable and effective devices for cleaning flue gases from the highly dispersed dust contained in them.

The dust content of the gases at the outlet of the electrostatic precipitator is 0.25-0.4 g/m3. If the filter is damaged (various defects in technical condition), the dust content of gases can reach 1-3 g/m3. (Smorodin et al. 2010, 70.)

Combination of electrostatic precipitators with a wet scrubber. At a significant number of RBIEPs, electrostatic precipitators is followed by scrubbing devices, which are the second stage of gas cleaning. Scrubbers make it possible to reduce the emission of sulfur dioxide and, under certain conditions, hydrogen sulfide into the atmosphere. It also make use of flue gases heat more effective. The scrubber (fig. 24) is a stainless steel tower, into the lower part of which flue gases are fed tangentially. In the upper part of the scrubber there is a battery of nozzles through which the irrigation liquid is supplied. To recover the heat of flue gases, a plate heat exchanger is installed, in which process water is heated. (Sivakov et al. 2015, 32.)

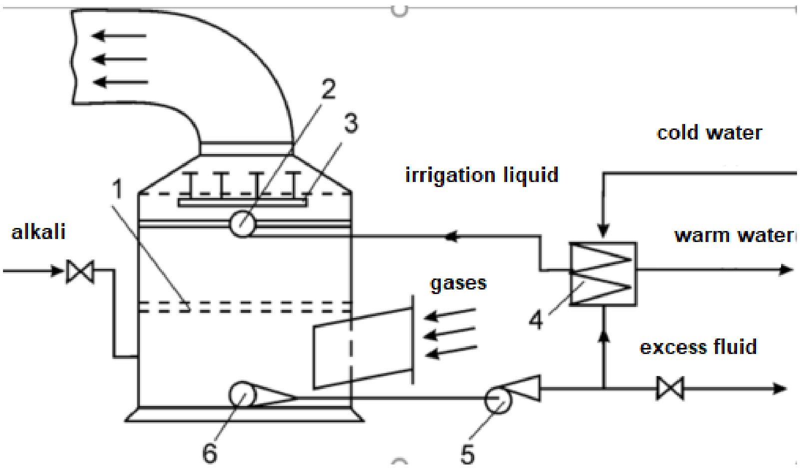

Figure 24: Hollow scrubber. 1 - gas distribution grid; 2 - a shower device; 3 - louvred droplet separator; 4 - heat exchanger; 5 - circulation pump; 6 - liquid outlet pipeline. (Smorodin et al. 2010, 72

Scrubber is involved in two stages of emissions reduction:

- *Second stage of dust removal.* Initially gasses flows through electrostatic precipitator, after which the density of dust is estimated around 0.25–0.4 g / m3 (for the electrostatic precipitator efficiency of 96–98%). Scrubber allows to clean out up to 66% of left dust particles (Smorodin et al. 2010, 72).

- *Flue gas deodorization.* The gases are washed in a scrubber with an alkaline solution. With direct contact of an alkaline solution with gases, the following reactions occur (Smorodin et al. 2010, 73):

  - **sulfur binding**
  - **CO2 binding**

  Simultaneously with absorption reactions, an interaction is possible between carbon dioxide (CO_2) and sodium sulfide (Na_2S), added with weak white liquor. The later one can be supplied as an absorption solution, or formed by soaking up hydrogen sulfide (H_2S) from flue gases. Sodium mercaptide resulting from the absorption of mercaptan can further decomposed. The decomposition of sodium sulfide and mercaptide leads to the release of hydrogen sulfide and mercaptan.

Utilization of steam and gas emissions from the smelt solvent. Heat losses with the vapour removed to the atmosphere from melt dissolving tank reach 4 - 5% of the potential heat of the liquor. For Recovery Boiler with a steam capacity of 100 t / h, the amount of heat loss with vapour is approximately 3.5–4.1 MW, or 0.59–0.67 GJ / t of produced cellulose. Losses of chemicals with evaporation for RBIEP of the specified capacity is 15 - 25 kg / h. (Andritz Oy 2020b.)

Utilization of steam and gas emissions makes it possible to use a significant proportion steam and gas heat, and drastically reduce the loss of chemicals. Devices that allow the simultaneous utilization of heat and chemicals from steam and gas emissions are quite common. Core components of such devices (Andritz Oy 2020b):

– heat exchanger washed by steam-gases with a temperature of 80-100℃

– drainage of condensate into the melt solvent tank in order to return the chemicals

– fan to increase the draft. In some cases only the natural draft of the exhaust pipe of the solvent tank is used. Then, a reduction in heat losses with steam and gases is achieved, while heating water in heat exchangers up to 50-55℃. In terms of capturing chemicals, such installations are still quite efficient (60 - 70%)

Figure 25 (Smorodin et al. 2010, 80) shows the scheme of steam-gas emissions utilization. Vapour from the melt solvent tank (6) is directed using a separate gas pipeline through the droplet catcher (9) to the suction of smoke exhauster (2). There they are mixed with the waste gases of the RBIEP. After smoke exhauster (2), gases enter the scrubber (10), where heating of the irrigation liquid takes place. The heat of scrubbing liquid is used to heat the process water up to 50 ° C in heat exchanger (1).

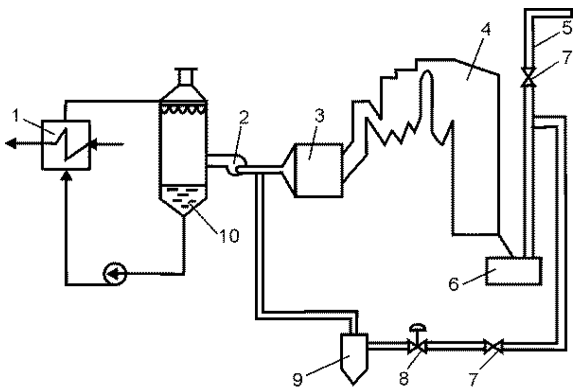

Figure 25: Scheme of utilization of steam and gas emissions. 1 - heat exchanger; 2 - smoke exhauster; 3 - electrostatic precipitator; 4 - Recovery Boiler; 5 - an exhaust pipe; 6 - melt solvent tank; 7 - shut-off valves; 8 - regulatory body; 9 - drop catcher; 10 - scrubber

The advantage of scheme is its simplicity. Steam and gas emissions stays at a level of 5-10% of RBIEP waste gases volumes. Smoke exhausters are usually designed with a large margin, that assure sufficient performance and prevent corrosion of walls. Due to mixing of flue gases with steam-gas emissions, temperature, partial pressures and composition of flue gases also hardly change. (Andritz Oy 2020b.)

Flue gas washing can be used to reduce sulfur dioxide emissions from the recovery boiler. Chloride is absorbed by cold water supplied to the flue gas supply. Chloride removal is usually 60-70%. Dust and SO_2 are removed in the washing area. Washing is carried out at a pH value of 6-7. The pH value is adjusted by feeding sodium lye, weak liquor, oxidized white liquor. SO_2 reacts with wash liquid to form Na_2SO_3 and Na_2SO_4. Sulfur-containing substances in the form of H_2S are removed together with SO_2 from the flue gases. High pH flushing fluid is required to remove hydrogen sulfide from flue gases. At a high pH value, nitrogen dioxide could also be absorbed, which is un-realizable due to the large amount of nitrogen dioxide generated during combustion. The collected flushing liquid is returned to the process, usually for white liquor preparation. (Andritz Oy 2020b.)

The flue gas washer can be installed on both new and existing installations, but it is always expensive. Thus even so this method of emissions reduction exists it is not feasible for RBIEP, burning high solids black liquor. (Andritz Oy 2020b.)

Application of selective non-catalytic reduction in recovery boiler. The process of denitrification of flue gases from nitrogen oxides is one of the existing processes using the basic principles of selective non-catalytic reduction to reduce NO_x emissions. The reduction of nitrogen oxides to nitrogen using ammonia occurs in accordance with the reaction equations (Andritz Oy 2020b):

$$2\,NO + 2\,NH_3 + \tfrac{1}{2}\,O_2 \longrightarrow 2\,N_2 + 3\,H_2O$$

$$3\,NO_2 + 4\,NH_3 \longrightarrow \tfrac{7}{2}\,N_2 + 6\,H_2O$$

When using amide of acetic acid, the following reaction occurs, as a result of which ammonia is formed:

$$2\,CO + H_2O \longrightarrow 2\,NH_3 + CO_2$$

In the process of this reduction, a boiler is used as a chemical reactor, which does not require the installation of additional equipment. These reactions takes place in a narrow temperature range (about 1000 °C). As the temperature rises, the formation of NO_x also increases. If the temperature is too low, ammonia is formed. The main parameter allowing to optimize and start the process of flue gas denitrification is ammonia (Minpriroda of the Republic of Belarus 2016, 72).

Efficiency of the flue gas denitrification process (Andritz Oy 2020b):

- the average level of NO_x emissions without flue gas denitrification is about 80 mg / Nm3
- the average level of NO_x emissions during denitrification of flue gases is about 55 mg / Nm3 (emission reduction is about 30%)
- increase in ammonia emissions by 3-4 mg / Nm3

Further emissions reduction is achieved by use of fully automated control system (featuring automatic combustion controller). It allows to monitor states of all processes online in real-time. This allows operators to react on any abnormal measurements in minimal time, that not only allows to reduce emissions, but also increase reliability and safety of production. (Andritz Oy 2020b.)

3.5.2 Company initiatives

Companies, that are involved in engineering and operation of units, producing noticeable levels of emissions, set specific targets and goals for development. They are used to identify what to strive for, what researches to prioritize and what processes can and should be improved. That targets can change with time to implement more strict requirements.

For example, Mondi Group was using a baseline of 0.59 tonnes of CO_2 per tonne since 2014. However, lately they stricken the requirement and settled a new target of achieving 0.25 tonnes of CO_2 per tonne by 2050. Actions, planned and already performed (according Mondi 2021a) to achieve this are:

- Implementing energy efficiency projects
- Substitution of fossil fuels with energy from biomass

- Building new recovery boilers, increasing the mill's energy efficiency and green energy generation (Syktyvkar in 2010, Frantschach in 2013, Ružomberok in 2014)
- Installing new turbine to reduce dust emissions, increasing power generation and green energy production (Stambolijski mill in 2013, Swiecie in 2015)

It is obvious that boiler modernization cause significant emission reduction. Reconstruction and upgrade of old boilers to implement technologies of RBIEP leads to lower emissions and higher energy production, that in turn make them more self-efficient and environment friendly.

Figure 26 and Table 2 (Andritz Oy 2020b) shows how the amount of emissions was reduced during last years in pulp and paper production. Particulate emissions from recovery boilers have decreased by 85% per ton produced.

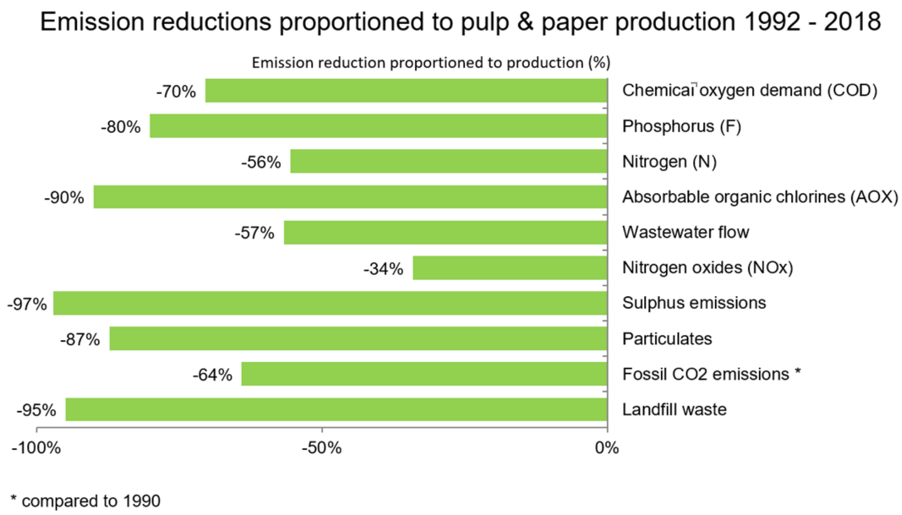

Figure 26: Emissions reductions in a period of 1992-2018, Andritz Oy

Table 2: Emission data slices by year

Flue gas emission	1982	1992	2002	2012
Uncombusted (CO), ppm	200	150	100	< 100
SO_2, ppm	600	200	10	< 1
TRS (H_2S), ppm	10	6	5	< 5
Dust, mg/m3n	300	150	100	< 20
NO_x, ppm	-	100	90	< 70
Total organic. (TVOC), ppm	-	60	60	< 20
Chlorine compounds (HCl), ppm	-	-	-	< 10

3.6 Energy generation

A RBIEP operates as a power plant in which concentrated black liquor is burned to produce heat used to generate high pressure superheated steam. Some of the energy contained in high pressure steam is used to generate electricity in a back pressure turbine. Medium pressure steam and low pressure steam are used to meet the heat demand in the sulphate pulping process. The electrical effect / thermal effect ratio is usually 0.2-0.3 (Ministry of the Environment of Finland 1997).

Pulp and paper mills are constantly looking for ways to increase the power output and efficiency of their steam generators. Produced energy can be used for own purposes or even sold out to the network. Tendency of energy production and consumption ratio can be seen on Figure 27.

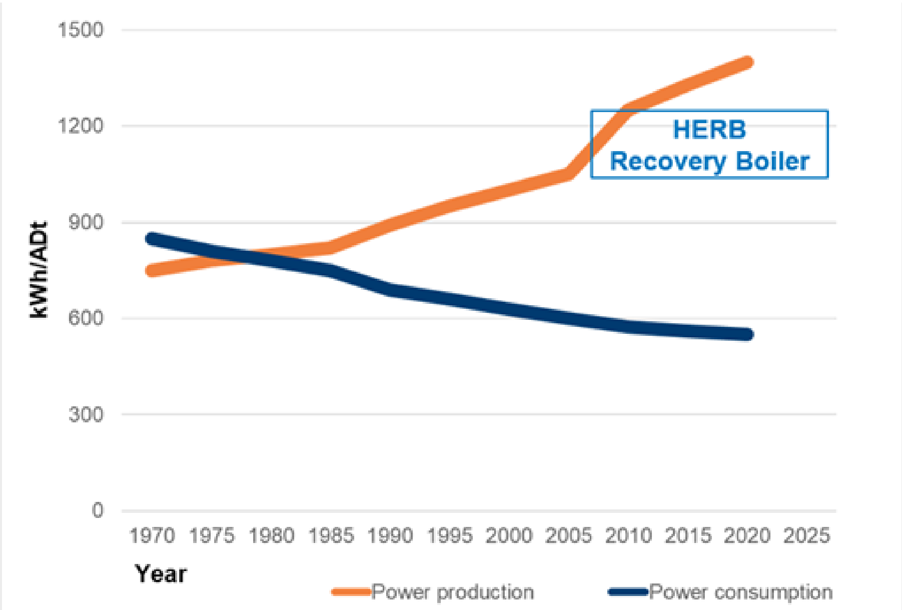

Figure 27: Comparison of power production and consumption (Andritz Oy 2020b)

Heat and electrical energy at the pulp mill is obtained mainly from the cooking liquor, remained after the manufacture of wood pulp. It is concentrated and burned in a RBIEP. After the combustion of organic substances, heat is released, which is transferred to the boiler pipes. As it moves through the pipes, water turns into steam. In the drum, water and steam droplets are separated using a separation device. Then the steam from the drum goes through pipes to a three-stage pre-heater, where it is superheated to the required temperature and is fed through the main steam header to the turbine compartment. Thermal energy of the waste gases formed during combustion is taken away, and, if it seems desirable, it is converted into electrical energy. The steam leaves turbine in the form of so-called exhaust steam. The heat contained in it is utilized by using it inside the pulp mill as motive steam in processes that require steam. If the pulp mill is part of a paper mill, there is generally no power generation for use outside the mill. (Andritz Oy 2020b.)

In case of Recovery Boiler with Improved Energy Production steam is supplied in such an amount that the generated heat and electricity exceeds the heat and electricity consumption of the plant itself. In this regard, in order to achieve a balance between energy production and its consumption, part of the generated heat must be used for the production. In addition to the electrical energy obtained from the turbine operating on waste steam and condensation electricity. (Andritz Oy 2020b.)

There are several ways to increase the power production from a Recovery Boiler with Improved Energy Production (Andritz Oy 2020b):

- increase the dry matter content of black liquor (fig. 28)
- air heating by steam extraction from a steam turbine
- withdrawing the soot-blowing steam from the extraction steam out of steam turbine rather than downstream of the primary superheater to recover more useful work from it
- in steam turbine plants with back pressure, no throttling of back pressure steam to increase the temperature of the feed (supplied) water
- installation of high pressure feed-water heaters using steam extraction from a steam turbine
- an increase in the temperature and pressure of the main steam (noting, however, that corrosion of the combustion chamber walls and in the area of the superheater growth as well)
- providing a re-heater design where the main steam, after expansion through the turbine, is sent back to the boiler for reheating before the next turbine stage
- using a steam condensing turbine instead of a back pressure steam turbine
- using the heat recovery from the electrostatic deposition trap to replace the back pressure steam typically used for preheating, and thus freeing the steam for use in power generation with the condensing turbine

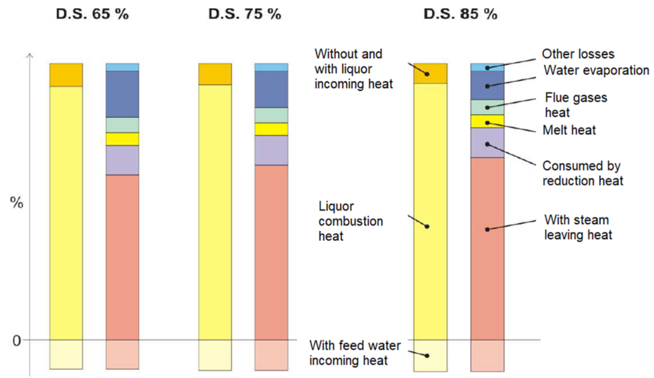

Figure 28: RBIEP Energy Levels by dry solids (D.S.) (Andritz Oy 2020b)

There are methods to increase energy production, but some of them still lead to increased corrosion of the lower furnace. For example, the vapour pressure in the wall of combustion chamber have to be kept low enough so that excessive corrosion does not occur in the water-cooled tubular walls. The potential for corrosion in the lower combustion chamber of waste heat boilers is a significant problem. Obviously, an improved boiler design that provides increased operating efficiency and power output while reducing the potential for corrosion will be welcomed by the industry. (Vakkilainen 2005, 10-6 - 10-9.)

3.7 Principles of sustainable development

Some of the sustainable development goals are to ensure healthy lives and promote well-being for everyone at all ages, to encourage sustained, inclusive and sustainable economic growth, full productive employment and decent work for all, to foster innovation, to decrease of fossil fuel consumption and to achieve the sustainable management and efficient use of natural resources, to take urgent action to combat climate change and its impacts. To achieve these global goals a highly efficient boiler that would help further close chemical cycle without increasing emissions is wanted. Innovated recovery boilers with renewable CO2-neutral energy as a by-product would help to (Andritz Oy 2020b):

- improve air quality and tackle climate change, where renewable energy production and energy efficiency combined with carbon capture are key actions (environmental benefit)
- decrease fossil fuels consumption (environmental and economical benefits)

– provide job opportunities for a large number of people (social benefit)

– achieve the highest power-to-heat-ratios from the recovery process (economical benefit)

Improving energy efficiency has always been a determining factor in energy development. To date, innovative technologies have been developed that optimize the use of both fossil and renewable fuels, as well as generated electricity. For example, complete utilization of all side streams of RBIEPs greatly improve self-maintainability of pulp and paper mill (fig. 29). But this is not enough to meet the ever-growing energy needs. Furthermore, energy system of the future must produce much less greenhouse gas emissions. (Andritz Oy 2020b.)

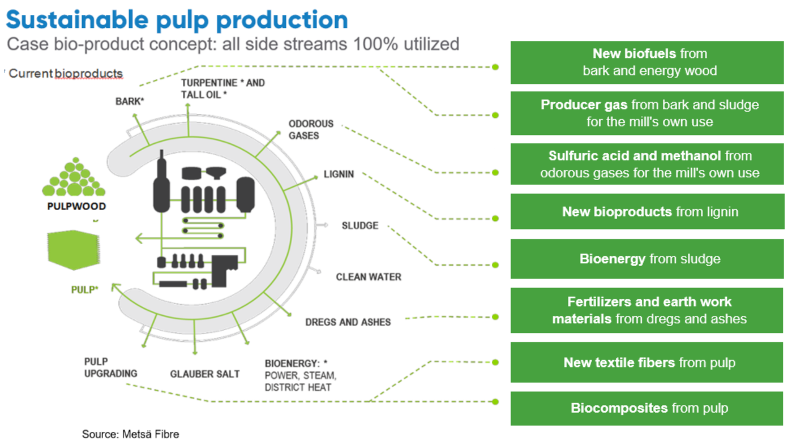

Figure 29: Side streams utilization on RBIEP (Andritz Oy 2020b)

Figure 30 shows the goals in accordance with 2030 Agenda for Sustainable Development (United Nations 2015), to which Andritz (as one of the RBIEP's manufacturer) is also committed in its own activities. Recovery Boiler with Improved Energy Production helps to achieve most of these goals.

Figure 30: The UN "2030 Agenda for Sustainable Development" (Andritz Oy 2020b)

3.7.1 Economic aspect of sustainable development in RBIEPs

Economic benefit is achieved through increasing of RBIEP power production. Higher levels of generated energy allows to decrease the need in external power supply. That, in turn, generates savings in operation costs. In context of pulp and paper mills that savings can reach millions of euros per year.

Recovery Boiler with Improved Energy Production concept implement several means for economic growth (Andritz Oy 2020b):

- utilize new technologies and equipments
- increase RBIEP energy production
- prefer equipment with low energy consumption
- efficient pulp washing with low water consumption
- low steam consumption by effective evaporation plants and optimized mill balance
- bark gasifying to replace fossil fuels in limekiln
- use energy recovery techniques
- improvement of product quality
- improvement in production efficiency and building overall production synergy
- investments into innovative researches and activities
- financial and economic feasibility that leads to good return on investment
- improving product quality and services that create sustained benefits for customers, society at large, and for the environment

3.7.2 Social aspect of sustainable development in RBIEPs

Energy production and use must not only be compatible with society's environmental priorities, but also be organized in such a way that it will support social cohesion. In many countries, there is an exacerbation of social problems and unclear prospects for the future. RBIEP creates a lot of new job opportunities, conditions for the professional and personal development of employees.

For pulp and paper mill in common and RBIEP particularly, main directions in satisfying the concept of social sustainability (Andritz Oy 2020b):

– *Significant amount of different job opportunities*: engineers, sales managers, expeditors, project assistants, operators, designers, builders, etc...

– *Science and education*: constant development of new technologies and knowledge, support for gifted schoolchildren, students and scientists.

– *Culture and self-development*: in recovery boilers of new generation is offered employees an attractive working environment with active development of human resources. Much attention is paid to the search and development of management personnel and young talents. As a lot of different nationalities can be interacted in boilers' design, building and operation, so respect for each national culture is required condition for working together.

– *Systematic improvement of the quality of life in the regions of operation*: building infrastructure and communication networks. Due to the large sizes of pulp and paper mills, they are usually built in places distant from existing inhabited areas. For example, in Uruguay construction site for a new mill is located deeply in forest area. For implementing this project a new railway and settlement is built.

– *Employee and contractor safety- and healthcare*: it's a moral and a business imperative to perform all needed actions to avoid harm to people. RBIEPs operate with high temperatures and pressures, as well as hazardous chemicals. Work on site is associated with high-risk activities that could affect people's safety and health. Thus, robust risk management controls and procedures to keep people safe are applied in engineering, construction and maintenance phases. Employees are more motivated and involved in operations as safer operations are more efficient and successful.

3.7.3 Ecological aspect of sustainable development in RBIEPs

Reasonable, caring attitude to resources, development of environmentally cleaner technologies, energy conservation, are becoming the main line of development of the planet as a whole. The production of clean energy is an increasingly pressing challenge to secure the future of humankind.

Industrial enterprises, which form the basis of modern production, are equipped rather often with outdated and worn-out equipment. Modernization of this equipment and improvement of treatment facilities are one of the important directions of their development.

The activities of environmental protection companies are aimed at (Andritz Oy 2020b):

- protection of water resources and optimization of water consumption
- reducing environmental impact and implementing initiatives to combat air pollution
- reduction of solid waste generation
- implementation of energy efficiency projects
- optimization of the supply chain

The pulp and paper industry can benefit more from resource efficiency programs than other industries. This is due to the high degree of resource consumption and the technological complexity of production in this industry. In terms of volume, more than 90% of emissions into the atmosphere of harmful substances at the cellulose enterprise are ash and dust, oxides of nitrogen, sulfur and carbon, as well as components of hydrocarbons. The specific emission of air pollutants from boilers per unit of generated electric power has slightly decreased in recent years. This decrease is associated with both the improvement of cleaning systems (including cleaning from ash in boilers). Another point is that reduction of water, wood and electricity consumption leads to significant savings and increases operational efficiency. (Andritz Oy 2020b.)

In many pulp and mill companies existing recovery boilers are being technically re-equipped or new Recovery Boiler with Improved Energy Production are built using technologies that are capable of ensuring proper treatment of air emissions. Furthermore, new equipments can operate on substances, treated as waste. E.g. In January 2019, within the framework of the project for the modernization of JSC Segezha PPM, a modern recovery boiler began operating at the plant, producing steam by burning wood waste. Plant receives additional electrical energy for production needs and at the same time it solves the problem of waste disposal. (Segezha Group 2021.)

One of the key points of RBIEP is use of modern ElectroStatic Precipitator. That allows to significantly reduce dust emissions into the atmosphere. Even so dust is not a direct greenhouse gas, reduction of its emissions has a clear advantage for surrounding environment.

Manufacturers and operators of pulp and paper mills can estimate their emission values on basis of EPC projects. Engineering, Procurement and Construction (EPC) is a particular form of contracting arrangement used in some industries, where the contractor carries out all or one of the types of work independently. The customer, in turn, carries out supervisory and verification activities. For example, Andritz Group is committed to sustainable development targets (Andritz Oy 2021). Due to the standardization of core processes, all its plants and systems comply with the highest environmental standards. Figure 31 shows their statistics on emissions per EPC project.

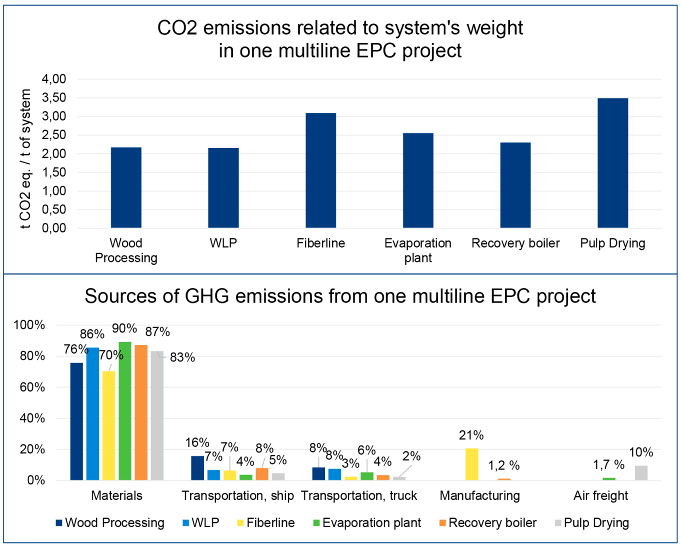

Figure 31: Emissions values and sources per EPC project, by Andritz Oy

4 RESEARCH OBJECTIVES

The pulp and paper industry, one of the leading branches of the forestry complex, combines technological processes for the production of cellulose, paper, cardboard and paper and cardboard products (writing, book and newsprint paper, notebooks, napkins, technical cardboard, etc.). In terms of its impact on the environment, this industry remains one of the most problematic in terms of the amount of toxic emissions into the atmosphere and discharges into water, and an environmental hazard to the natural environment. In addition, a distinctive feature of pulp mills is outdated equipment and technological process. (Lyapina 2017, 47-48.)

Recovery boiler plays an essential role in the production of pulp and paper products. The quality of its work depends on how environmentally friendly the process of chemical regeneration during cooking sulphate pulp will be. The new recovery boilers are made in accordance with global environmental standards and the best available technologies (BAT) in the field of ecology, as well as have increased power generation.

The relevance of this thesis lies in highlighting the methods used in production to reduce harmful effects while guaranteeing the receipt of more energy, which can, for example, be directed to the production of electricity. It also presents how high power production results in a strong economical benefit, expressed in saving of millions of euros for owners if pulp mill.

The aim of this thesis is to study the recovery boiler with improved energy production, its emissions, in particular Äänekoski mill recovery boiler of new generation as an example of technologies following environmental protection programs within the framework of sustainable development. Another aim is to calculate and prove RBIEP's economic benefits.

To achieve these goals, it is necessary to solve the following main tasks:

- analyze the emissions of pollutants into the atmosphere
- review boilers' technologies for the production of CO2 neutral energy
- review possibility of increasing steam production
- compare RBIEP's steam production and emission factor with other kind of boilers
- calculate RBIEP's operational savings in comparison with conventional recovery boilers

5 MATERIALS AND METHODS

The main method, used in this thesis, to prove RBIEP's energy efficiency and clean energy production is compare emission factor of recovery boilers of new generation and other industrial steam boiler.

5.1 Emission factor

RBIEP manufacturing companies measure emissions only during warranty tests. Customers (in fact, users) usually do not publish emission of recovery boilers separately from entire pulp mill. For the calculations it is assumed that CO_2 emissions from recovery boilers represent approximately 78% of total pulp mill emissions Yang et al. 2021, 14.

Knowing annual power generation (P_{annual}) and total mill CO_2 emissions (E_{CO2}) we can calculate power-to-CO_2 emission factor (E_{factor}) as:

$$\mathrm{E_{factor}} = \mathrm{P_{annual}}/\mathrm{E_{CO2}} \tag{3a}$$

The ratio of steam to energy conversion is as following: 3.53 lbs of water evaporated at 212 ℃ can be converted into 1 KW (Thermoflo Equipment Company, Inc 2013). Thus hourly energy generation P_{hourly} can be calculated from steam production in lb/h $SP_{lb/h}$. Assuming that facility operates **24 h/day** for **365 days/year** annual power generation (P_{annual}) can be calculated as following:

$$\mathrm{P_{hourly}} = 1kW * \mathrm{SP_{lb/h}}/3.53lb/h \tag{4a}$$

$$\mathrm{P_{annual}} = \mathrm{P_{hourly}} * 24h * 365days \tag{4b}$$

5.2 Data sources

Data of steam production for each kind of considered boilers (RBIEP, conventional RB, fossil fuel and biomass boilers) was published in official web-sites of companies-owners and companies-manufacturers. As they were official sources, can be stated that data is reliable and trustworthy.

Used in calculations data of CO2-emissions for mills was presented in annual reports of companies-owners (Metsä Group, JSC "Kirovogradoliya") and was calculated for conventional recovery boiler based on fuel consumption published in report of company-owner (Ilim Group).

Conversion factors for the ratio of steam to energy was taken from engineering conversion tables, providedthe multiplying factors necessary to convert one unit of measurement to another.

6 RESULTS

In this thesis principals of Recovery Boiler with Improved Energy Production operation, main sources of emissions and ways of their reduction were reviewed. For the purpose of estimation this technology effectiveness, annual energy production (P_{annual}) and CO_2 emission factor (E_{factor}) were calculated. Carbon dioxide (CO_2) is considered the most important greenhouse gas of anthropogenic origin. Its impact to greenhouse effect is significant. Other anthropogenic emissions (SO_2, NO_x, TRS, dust) also affect the integrity of global and local ecosystems and directly impact the health of billions of people, but their influence greenhouse effect is indirect (fig. 32).

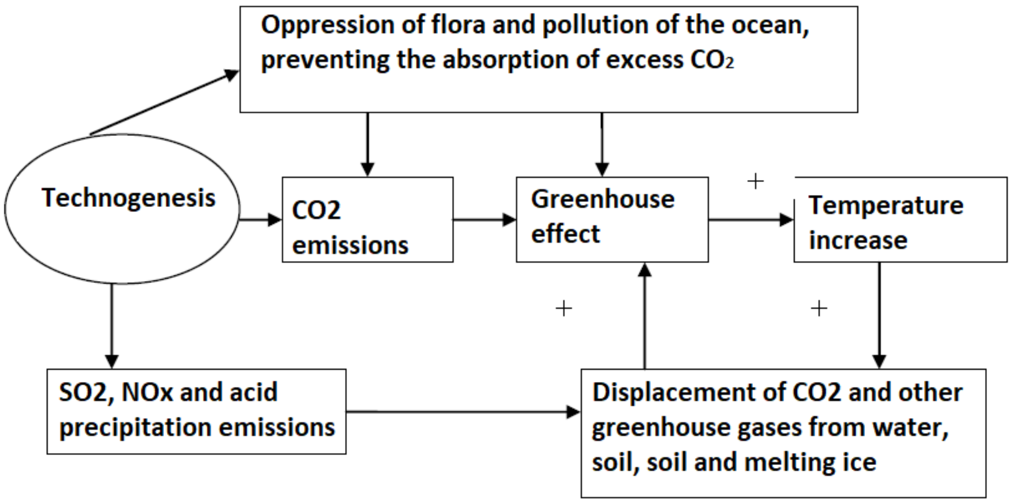

Figure 32: Violation of biotic regulation of the carbon cycle and self-acceleration of the greenhouse effect (Studme 2021)

For example, a nitrogen dioxide molecule ejected from a CHP chimney can end up in forests or freshwater bodies in the form of a nitrous acid molecule that kills aquatic life and insects.

As all emissions from RBIEPs affect negatively on environmental, they were described in the thesis as well as ways to their reduction. However, they were not taken into account when evaluating the effectiveness of the applied technologies, since they are not treated as direct GHGs.

In this work, only CO_2 emissions were taken into account. And only CO_2 fuel part of emissions was used in calculations, as biofuels are environmentally neutral - when burned, exactly as many chemicals are released as were synthesized during the formation of biomass. CO_2 emissions from biofuels combustion do not increase the greenhouse effect. As a consequence of using only CO_2 fuel emissions, Biomass boilers emission factors cannot be calculated using same approach as for other types of boilers.

The total amount of generated energy depends on the size of the boiler and fuel load. By their increasing, power generation will increase too. But it must be borne that amount of emission will increase as well. Thus emission factor is more reliable metric for comparison different recovery boilers effectiveness. It determines the amount of power produced per unit of emissions.

6.1 Calculating emission factors and power generation

For effectiveness comparison several alternative energy producing installations were selected and calculated using the same approach as for RBIEP:

- Conventional Recovery Boilers - predecessors of RBIEP
- Fossil Fuel Boilers - traditionally strong source of GHG-Emissions
- Biomass Boilers - opposed to Fossil Fuel Boilers, CO_2 neutral

6.1.1 Äänekoski recovery boiler of new generation (RBIEP)

For the purpose of comparison of what RBIEP can provide with other energy generation technologies we will use the case of Äänekoski recovery boiler. This mill is equipped with most innovative features and thus maximize the use of bioenergy. It produce 2.4 times more energy then it consumes. Overall annual electricity production represents 2.5 per cent of all electricity production in Finland (Valmet 2021). This case is a good example of current technologies capabilities.

Äänekoski recovery boiler implements following technologies considered in the thesis (Valmet 2017, 4-7):

- air connections at distinct levels and locations (including a quaternary air level)
- cleaning of flue gases in electrostatic precipitators (flue gas cleaning)

– scrubber

In this boiler DNCG and other side streams coming from other parts of the mill are burned that cause minimizing odorous gas emissions from mill. In addition it also use several high-power yielding techniques, methodologies and equipments (Valmet 2017, 5):

– high black liquor dry solids

– air and DNCG preheating

– fully pressurized feedwater tank

– heat recovery from vent gases

– heat recovery from flue gases

– high main steam parameters

All together these features allows to significantly increase energy production of the boiler (see chapter 3.6).

Äänekoski mill has one Recovery Boiler with Improved Energy Production. Its parameters according Valmet 2017, 5-6, 10 are presented in a Table 3 .

Table 3: Äänekoski mill. RBIEP parameters

Capacity	7200 tds a day
Feed water temperature	183 ℃
Working pressure	110 bar
Working temperature	515 ℃
Steam production	363 kg/s

Steam production is **2880997 lb/h**. Using formulas 4a and 4b yearly power generation is:

$$\mathrm{P_{annual}} = 2880997 lb/h * 1kW * 24h * 365 days/3.53 lb/h = 7.14 TWh$$

Table 4 presents emissions from Äänekoski mill reported in 2020 (Metsä Group 2020). CO2 bio is not treated as a source of additional carbon in atmosphere, so we will

Table 4: Äänekoski mill. Annual emissions for 2020

CO2 bio	3177.108 t
CO2 fuel	49.105 t
SO_2	0 t
TRS	0 t

calculate only CO2 fuel related emission factor. The CO_2 emissions from recovery boilers represent approximately 78% of the total mill emissions (Yang et al. 2021, 14).

Emission factor for Äänekoski RBIEP calculated using formula 3a:

$$\mathrm{E_{factor}} = 7.14TWh/(49.105tCO2 * 0.78) = 186.66GWh/tCO2$$

6.1.2 Danstoker boilers

This company produce a variaty of so-called Biomass Boilers, which operate on various types of fuel, regardless of its shape and density (combustible raw materials of plant origin). This raw material can be immediately used to generate heat in biofuel boilers or is a derivative for the production of briquettes or pellets. Biofuel boilers have a shaft-type structure, combustion occurs in the lower layer. Biomass boilers are used in: the production of heat energy for heating industrial premises, large retail areas, agricultural enterprises, nurseries, heating systems and central heating systems for public buildings and villages; cogeneration of heat and electricity, production of steam for industrial processes. (Danstoker 2021.)

Biomass boilers are assumed to be CO_2 neutral, as their emissions consists of CO_2 bio. As it was discussed in 3.4.4 this emissions are not treated as a source of additional carbon in atmosphere, as carbon dioxide produced when burning organics is assumed to be reabsorbed back to organic matter in forests.

Danstoker biomass boiler product line contains solutions with a very wide support of renewable energy sources (Danstoker 2021). Assuming product with maximum available design pressure up to **43 bar** and steam production rate of **68 t/h** (= 149914 lb/h), using 4a and 4b:

$$\mathrm{P_{annual}} = 149914lb/h * 1kW * 24h * 365days/3.53lb/h = 0.37TWh$$

6.1.3 Wuxi Xineng biomass boilers

Wuxi Xineng Boiler Co. is another company manufacturing Boimass Boilers and pressure vessels. Presented biomass steam boilers implements several energy-efficient technologies: double row of coil structure, efficient air pre-heater and heat absorbing in the boiler tail arrangement. Boilers are made of high quality thermal insulation material and have small heat loss. They works on straw, rice husks and other combustible substances. Rated steam capacity is **2-20 ton/h**, at working pressure **1.25-2.5 Mpa** and steam temperature **193-226 ℃**. Max steam capacity - **20 t/h** (Wuxi Xineng 2021b).

$$\mathrm{P}_{\mathrm{annual}} = 44092.4lb/h * 1kW * 24h * 365days/3.53lb/h = 0.11TWh$$

6.1.4 Reserve gas boiler at the oil extraction plant of JSC "Kirovogradoliya", Ukraine

This boiler is an example of Fossil Fuel Boilers. Such industrial steam boilers are manufactured for burning coal and brown coal, natural gas, fuel oil, diesel fuel. Modern industrial gas steam generators are equipped with electronic devices that control all processes and carry out monitoring, which increases the safety of installation. However, due to used fuel, levels of emissions cannot be effectively decreased. (Ruffell 2021.)

Oil extraction plant of JSC "Kirovogradoliya" features 2 permanent boilers in addition to reserve one. Reserve boiler is turned on during maintenance operations (approximately 1 month every year). It works on natural gas and features steam production of **16 t/h** (equals **35273.6 lb/h**). CO_2 emissions from burning natural gas in a reserve boiler during overhaul of working boilers in 2012 is reported as **2165 tCO2** (Kramar 2012, 7, 12).

Considering that this boiler was working 1 month during the year, the approximate annual emissions would be **25980 tCO2**. Corresponding energy production and emission factor values are:

$$\mathrm{P}_{\mathrm{annual}} = 35273.6lb/h * 1kW * 24h * 365days/3.53lb/h = 87534.47MWh$$

$$\mathrm{E}_{\mathrm{factor}} = 87534.47MWh/25980tCO2 = 3.37MWh/tCO2$$

6.1.5 Kawasaki Advanced Clean Combustion Boiler

Another example of Fossil Fuels Boilers. It burns heavy fuel oil with a high fuel nitrogen content in a furnace consisting of a high temperature combustion / reduction zone and a low temperature oxidation zone. The system is effective on bitumen and conventional oil.

It is designed to reduce NO_x and dust emissions. It is achieved by dividing combustion process into two subprocesses. Lower part of a chamber has a high temperature about 1500 - 1800 ℃. It is used to gasify heavy oil. The upper half of a chamber on contrary is low-temperature area where oxidation happens. Combination and aligning sizes, temperatures and other conditions of burning chamber areas allows to achieve high efficient combustion process with NO_x emissions of less than 100 ppm and less than 250 mg/Nm3. (Kawasaki 2021a.)

According Kawasaki 2021a the maximum steam production of KCCEB is **200 t/h** (equals **440924 lb/h**).

$$\mathrm{P_{annual}} = 440924lb/h * 1kW * 24h * 365days/3.53lb/h = 1.1TWh$$

6.1.6 High pressure steam boiler Wuxi Xineng Boiler Co.,Ltd.

Fossil Fuel Boiler using natural gas, heavy oils, light oils, municipal gas and/or methane as a fuel. The boiler provides heat and is used to heat rooms, apparatus and pipelines, as well as to rotate turbo machines for electricity generation. Product line include solutions with steam production **6-100 t/h** and working pressure **1.25-9.82 Mpa** (Wuxi Xineng 2021a).

Taking max steam productivity of **100 t/h** (equals **220462 lb/h**):

$$\mathrm{P_{annual}} = 220462lb/h * 1kW * 24h * 365days/3.53lb/h = 0.55TWh$$

6.1.7 Boiler N14 in a power plant in Bratsk

This is a Conventional Recovery Boiler. It ensures the utilization of wood waste, the generation of heat and electricity for the production needs of the plant, neighbouring woodworking and wood-chemical enterprises. The nominal parameters of live steam (Ilim Group 2009, 11):

– pressure: **3.9 MPa**

– temperature: **440 °C**

– steam capacity: **75 t/h** (equals **165346.5 lb/h**)

– fuel consumption: **2986 GJ**

– CO_2 emission factor for fuel oil: **0.0774 tCO2-eq./GJ** (IPCC 2007, Table 2.2)

$$\mathrm{P_{annual}} = 165346.5lb/h * 1kW * 24h * 365days/3.53lb/h = 0.41TWh$$

Using formulas for calculation annual CO_2 emissions ($BERFO_y$) from fuel oil combustion in boiler during the year (Ilim Group 2009, 24, 59):

$$\mathrm{BERFO}_y = 2986GJ * 0.0774tCO2/GJ = 231tCO2 - eq$$

Corresponding emission factor:

$$\mathrm{E_{factor}} = 0.41TWh/231tCO2 = 1.8GWh/tCO2$$

6.2 Calculated values comparison

Values, received in calculations, can be seen in Table 5.

Table 5: Calculated boiler parameters

Considered boiler	Type	P_{annual}, MWh	E_{factor}, MWh/tCO2
Äänekoski mill	RBIEP	7149443	186660
RB N14 in a power plant in Bratsk	Conventional	410321.6	1776.3
Reserve gas boiler at JSC "Kirovogradoliya"	Fossil fuel	87534.47	3.37
Danstoker boilers	Biomass	372024.5	-
Wuxi Xineng boilers	Biomass	109419.1	-

Figure 33 shows that in terms of emission factor, RBIEPs surpass other types of boilers. Its emission factor is significantly higher then others.

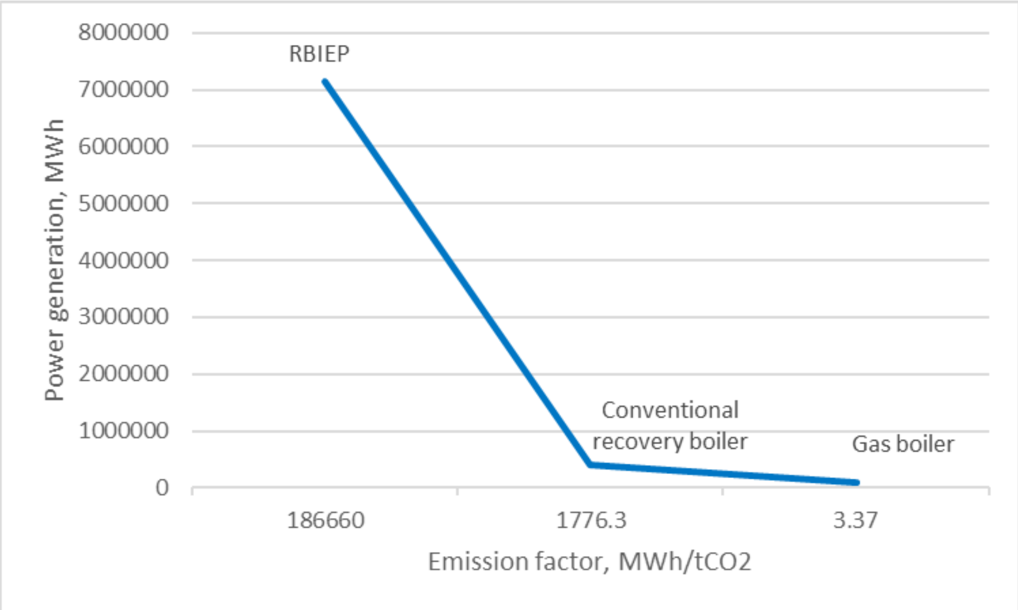

Figure 33: Power generation and emission factor in boilers

Figure 34 shows how boiler steam generation has increased compared to traditional recovery boilers (Valmet 2017).

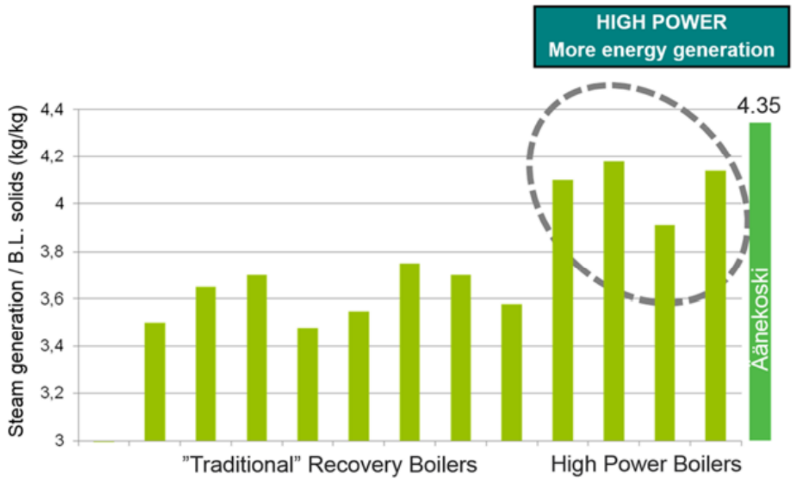

Figure 34: Steam generation ratio in different types of recovery boilers (Valmet 2017)

It is not possible to compare RBIEP with Biomass boilers using the same scheme, due to the biomass technologies used. However, if we return to energy production, RBIEPs are capable of producing much more energy (fig. 35).

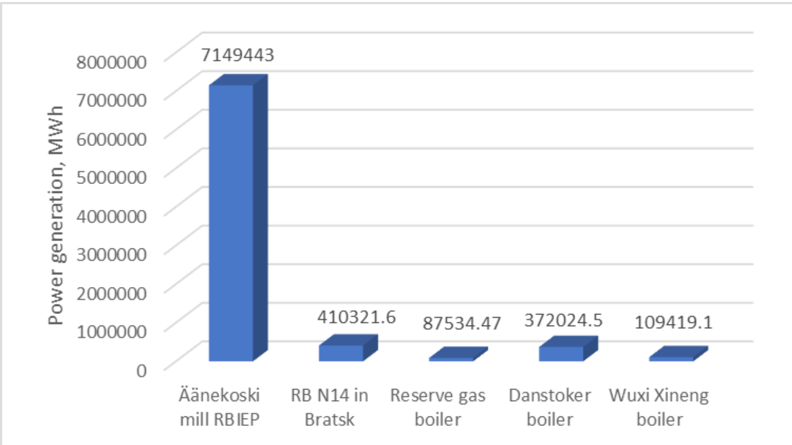

Figure 35: Power generation in boilers

7 DISCUSSION AND CONCLUSION

7.1 Evaluation of the results

Calculations shows that installations, implementing RBIEP techniques features a significantly larger emission factor value. That means that they have much higher power production and lower amount of CO_2 emissions, emitted in result of fossil fuel usage as auxiliary energy source during startup shutdown, upsets or for extra steam production.

RBIEP is distinguished by ability to reduce emissions and increase steam output thanks to improved technologies. These boilers, on the one hand, increase the efficiency of dust collection and emission reducing while increasing productivity, and on the other hand, provide the enterprise with its own energy resource. Generated in RBIEP energy makes it possible to transfer mill to self-sufficiency, and in some cases to supply surplus to the power grid.

For the pulp and paper industry, the topic of ecology and environmental protection has always been important. The environmental friendliness of production has long been a factor in competition on the world market for pulp, paper and cardboard. Today enterprises seeking leadership in determining the development of the industry must meet the most stringent environmental requirements, including the requirement to reduce greenhouse gas emissions.

RBIEP plays an essential role in the production of pulp and paper products. The quality of its work depends on how environmentally friendly the process of chemical regeneration during cooking sulphate pulp will be. Boiler do not only provide combustion of highly concentrated gases, but also provides the pulp mill with sufficient energy.

At the moment, RBIEP is not completely CO_2-neutral. These boilers require usage of fossil fuels at least in the start-up process. In the event of malfunctions, repairs or other works on boiler maintenance, the number of moments when CO_2 fuel is released increases. The term "CO_2-neutral" can be used to describe the normal operation of the when the process is started and the equipment is normally working. However, when compared with traditional boilers, it is clear how big a leap has been made in terms of reducing environmental impact. Further developments can make it even better. Trends in the reconstruction of existing installations and the development of new technologies give rise to the hope that in the future,CO_2 fuel emissions during maintenance will be minimized, or even eliminated altogether. That will allow such boilers to be considered completely CO_2-neutral.

It also worth noting, that RBIEP consumes mostly black liquor as a fuel. In turn, black liquor is a waste from pulp and paper production. In case if recovery boiler is excluded from pulp mill processes, this type of waste will require correct utilization. Thus, RBIEP not only supply energy and allows to recover some required chemicals, but also recycle by-product chemicals of kraft process.

7.2 Future perspectives and research needs

Research can be repeated in several years - technologies are advancing, mills are reconstructed. Companies set own goals on emissions reductions (up to 2025, 2030 etc.) - so in several years it can be reviewed the state of the industry.

Some examples of climate programs in companies producing, servicing and using recovery boilers, that can be reviewed:

- Ilim Group (the leader in the Russian pulp and paper industry). An important area for the period 2021-2027 is the implementation of a program to improve environmental efficiency as part of the transition to BAT in recovery boilers, including the reduction of discharges of pollutants and the organization of an automatic control system for emissions. (Ilim Group 2020.)
- Mondi Syktyvkar (the largest Russian paper producer). Science-based targets to 2025 and 2050 are to reduce GHG emissions 34% per tonne of saleable production by 2025 and 72% per tonne of saleable production by 2050, from the 2014 baseline. Another goal is to reduce GHG emissions by 39% per MWh by 2025 and by 86% per MWh by 2050, from the 2014 baseline. (Mondi 2020.)
- Valmet (a manufacturer of equipment, automation solutions and services for the pulp and paper industry and energy). It targets to reduce to 20% energy use of own current technologies and providing 100% carbon neutral production for all pulp and paper industry customers by 2030. (Valmet 2020.)

One more direction for further researches is evaluation of emissions and environment impact at the process of construction. Pulp and paper mills and Recovery Boilers requires large amount of materials, equipments and supplies to be originally constructed.

Need to take into account emissions and negative impact on environment during construction. It is necessary to consciously approach the regulation of emissions during the production of construction works, provided that different works are carried out at different times, and the equipment does not work simultaneously. Taking into account the sequence and simultaneity of processes makes it possible to assess the real impact of construction work on the population. As well as atmospheric pollution by chemical and physical factors that is organoleptically felt, which is especially important for construction carried out on the territory of cities.

7.3 Conclusions

The aim of the study was to analyse boilers' technologies for the production of clean energy, to compare RBIEPs energy production and emission factor with other kind of boilers. It was proved that RBIEPs produce significantly more energy than conventional recovery boiler, fossil fuel and biomass boilers. Amount of emissions taking into account full cycle of boiler processes are higher then Biomass boilers, but much less then Fossil Fuel ones.

I think, the trend for improving boiler effectiveness will continue in next years. Even if to exclude environment benefits, raised from that, there is a great economical benefit - savings can reach millions of euros per year. That gives businesses a strong reason to continue researches with following renovations and modernizations. Companies already invest in environmental projects that will help reduce CO_2 emissions globally, thereby offsetting the amount of CO_2 that is still emitted during production. For instance, in 2019, Mondi (one of the companies using RBIEPs in their mills) was able to reduce its CO_2 emissions by 15.5%. To offset emissions that they cannot reduce through other measures, Mondi is partnering with ClimatePartner to finance and maintain a hydropower plant in southern Brazil (Mondi 2021b).

Climate change is the most serious crisis of our time, and it is happening even faster than we thought. We need to systematically reduce CO_2 emissions to the atmosphere. Switch to green technologies and improving energy efficiency of industries is right path to stop climate changes. Advanced development and use of renewable energy sources will enable us all to take the leap towards a cleaner and more sustainable world.

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Real emissions (dry, 6% O_2)

Table A1: Reported emission from modern RBIEPs

	Steam production, t/h	Emission	mg/ Nm3
RBIEP Kawasaki[1]	475	Dust	10
RB-1750, Ilim Group, Bratsk	254[2]	Dust	50[3]
RBIEP Äänekoski mill[4]	1306.8	NO_x	200

Table A2: Emission from non-RBIEP industrial stream boilers

	Steam production, t/h	Emission	mg/ Nm3
Bubble fluidized bed boilers[5]	662.6	NO_x Dust	<453[6] 17.5
Kawasaki Advanced Clean Combustion Boiler[7]	200	NO_x	<250

[1] Kawasaki 2021b
[2] Volodeev 2021, 107
[3] Ilim Group 2020
[4] Valmet 2017, 5, 10
[5] Foster Wheeler 2021
[6] Converted to mg/Nm3 acc. table 2.4 in Stewart 2012
[7] Kawasaki 2021a